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PB-280 657

Full-Scale Demonstration of Nitrogen Removal by Breakpoint Chlorination

Sacramento Regional County Sanitation District, Calif

Prepared for

Municipal Environmental Research Lab, Cincinnati, Ohio

Mar 78

United States
Environmental Protection
Agency

Municipal Environmental
Research Laboratory
Cincinnati OH 45268

EPA-600/2-78-029
March 1978

PB 280 657

Research and Development

EPA

Full-scale Demonstration of Nitrogen Removal by Breakpoint Chlorination

Environmental Protection Technology Series

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/2-78-029		PB280657

4. TITLE AND SUBTITLE	5. REPORT DATE
FULL-SCALE DEMONSTRATION OF NITROGEN REMOVAL BY BREAKPOINT CHLORINATION	March 1978 (Issuing Date)
	6. PERFORMING ORGANIZATION CODE

7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
Richard W. Stone Sacramento Area Consultants	

9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Sacramento Regional County Sanitation District 4660 Ecology Lane Sacramento, California 95827	1BC611
	11. CONTRACT/GRANT NO.
	S803343-01

12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
Municipal Environmental Research Laboratory--Cin.,OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, Ohio 45268	Final
	14. SPONSORING AGENCY CODE
	EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: James J. Westrick (513) 684-7652

16. ABSTRACT

A large-scale breakpoint chlorination system was constructed and operated at Rancho Cordova, CA. Reliable operation was demonstrated and a number of observations regarding process chemistry and engineering were made, including (1) the chlorine to ammonia-N ratio required to reach breakpoint and to maintain a controllable free residual was 10:1; (2) nitrate production was not pH sensitive in the range 6.5 to 8.5; (3) the rate of reaction of ammonia oxidation varied with final pH, with fastest rates observed at pH 7.0. Slower rates were observed at lower and higher pH; (4) mixing intensity had no effect upon chemical requirements or effluent quality, but was important for smooth process control; (5) the amount of sodium hydroxide used for neutralization was identical to that predicted from stoichiometry; (6) the control system used here provided excellent control of the process chemistry.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Chlorination Ammonia Oxidation Waste treatment Process control Reaction time	Demonstration Rancho Cordova	13B

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release Unlimited	Unclassified	80
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	A05-A01

EPA Form 2220-1 (9-73)

★ U.S. GOVERNMENT PRINTING OFFICE: 1978—260-880/58

EPA-600/2-78-029
March 1978

FULL-SCALE DEMONSTRATION OF NITROGEN REMOVAL BY BREAKPOINT CHLORINATION

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FOREWORD

The Environmental Protection Agency was created because of increasing public and government concern about the dangers of pollution to the health and welfare of the American people. Noxious air, foul water, and spoiled land are tragic testimony to the deterioration of our natural environment. The complexity of that environment and the interplay between its components require a concentrated and integrated attack on the problem.

Research and development is that necessary first step in problem solution and it involves defining the problem, measuring its impact, and searching for solutions. The Municipal Environmental Research Laboratory develops new and improved technology and systems for the prevention, treatment, and management of wastewater and solid and hazardous waste pollutant discharges from municipal and community sources, for the preservation and treatment of public drinking water supplies, and to minimize the adverse economic, social, health, and aesthetic effects of pollution. This publication is one of the products of that research; a most vital communications link between the researcher and the user community.

This report summarizes the results of a demonstration program which was carried out to establish design and operating criteria for breakpoint chlorination nitrogen removal systems for use in municipal wastewater treatment applications. The development and demonstration of such processes provides additional tools for use by water pollution control agencies in their efforts to maintain and enhance the quality of the environment.

Francis T. Mayo, Director
Municipal Environmental Research Laboratory

ABSTRACT

This work constitutes the first large-scale demonstration of breakpoint chlorination for removal of ammonia nitrogen from municipal wastewater. The report includes a discussion of breakpoint chlorination process chemistry, an evaluation of chemical consumption, and recommendations for process control.

Breakpoint chlorination can occur in wastewater effluents following addition of sufficient chlorine for the oxidation of ammonia nitrogen to, principally, nitrogen gas. Theoretically, 7.6 mg/l of chlorine are required for the conversion of 1.0 mg/l of ammonia nitrogen to nitrogen gas. In the breakpoint chlorination process evaluation at Rancho Cordova, an average dosage of 10 mg/l chlorine was required for the conversion of 1.0 mg/l ammonia nitrogen to nitrogen gas. The difference between theoretical and actual chlorine dosages was found to be largely due to chlorine consumption from the oxidation of ammonia nitrogen to nitrate nitrogen, a competing side reaction with a less desirable end product. Overall, about 96 percent of the chlorine dosed to the Rancho Cordova system was accounted for in reactions between chlorine and nitrogenous species in specific, identified chemical pathways, and free chlorine residual remaining in solution following breakpoint.

Tests with mechanical mixing devices showed that mixing intensity at the point of chemical addition had little effect on chemical consumption and efffluent quality. The rate of the breakpoint reaction was found to vary depending upon the system pH, with fastest rates at a pH of 7.0. At pH 7.0, about 60 sec to 90 sec elapsed between chemical addition and completion of the chemical reactions. The Rancho Cordova evaluation showed that the process requirement for alkalinity supplementation (pH control) was almost exactly equal to that predicted from the chemical stoichiometry. A compound loop control strategy was recommended for dosage control of chlorine and alkalinity supplement.

This report was submitted in fulfillment of Grant No. S-803343-01-0 by Sacramento Area Consultants for the Sacramento Regional County Sanitation District. The project was carried out under the sponsorship of the U.S. Environmental Protection Agency. This report covers work completed as of June 30, 1977.

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SECTION 1

INTRODUCTION

Chlorination can be used to remove ammonia nitrogen from wastewater. It requires the addition of chlorine, and makes use of the rapid, specific reactions between chlorine and ammonia in dilute aqueous solution which can lead to the oxidation of ammonia to nitrogen gas and other end products. The term "breakpoint" has been applied to the process because a point of minimum chlorine residual occurs at the chlorine dosage required to complete the chemical reaction.

Testing of breakpoint chlorination for nitrogen removal from sewage has, to date, largely been carried out in small pilot-scale systems. Data on breakpoint chlorination from pilot-scale systems have contributed greatly to our understanding of process chemistry, but actual application data and design criteria for full-scale breakpoint systems have not been readily available to the design engineer and planner. The work discussed here was carried out to provide information and design recommendations from a full-scale breakpoint chlorination system in the specific areas of process control techniques and instrumentation, chemical consumption, and breakpoint reaction end products. The system tested during this program was designed to accept variations in flow rates and chemical composition which are characteristic of effluent from nonnitrifying secondary wastewater treatment plants.

The full-scale demonstration of breakpoint chlorination was carried out at Rancho Cordova, California, between December, 1975 and March, 1976. Costs of the evaluation were borne jointly by the U.S. Environmental Protection Agency, the Sacramento Regional County Sanitation District and the State of California.

SECTION 2

CONCLUSIONS

A full-scale breakpoint chlorination facility was constructed at the Rancho Cordova Sewage Treatment Plant in Rancho Cordova, California. The system was operated 24 hours per day, 5 days per week from December, 1975 until March, 1976. Process flow rates varied from about 0.1 mgd to 1.2 mgd. Influent ammonia nitrogen concentrations were ordinarily in the range of 15 mg/l to 25 mg/l.

Flexibility was incorporated into the breakpoint chlorination chlorine dosage and pH control systems to facilitate the testing of several control strategies. Data from automatic on-line analyzers and from laboratory analysis of samples collected manually provided the basis for process chemistry investigations.

A number of specific observations and conclusions made as a result of the Rancho Cordova breakpoint chlorination demonstration program are enumerated below:

1. The dosage of chlorine at Rancho Cordova required to reach breakpoint and maintain a controllable free residual in the process stream averaged 10 mg/l for each 1.0 mg/l ammonia nitrogen present in the process influent.

2. Approximately 70 percent of the breakpoint chlorine dosage was consumed to produce nitrogen gas (N_2) from ammonia (NH_4^+) at pH set points between pH 7 and 8. The oxidation of ammonia to nitrate consumed 8 percent to 19 percent of the total chlorine dosed to the system. Overall, about 96 percent of the total chlorine dosage was accounted for in reactions between chlorine and nitrogenous species in specific chemical pathways and free chlorine residual remaining in solution following breakpoint.

3. Nitrate (NO_3^-) production in breakpoint chlorination was not found to be pH sensitive, with about 1.0 mg/l of nitrate (as N) produced from ammonia across a final system pH range of pH 6.5 to 8.5. The production of

nitrate from nitrite was wholly dependent upon influent nitrite concentration.

4. Nitrogen trichloride production was observed to be fairly insensitive to pH across a range of final system pH values from pH 7 to 8. The median value for nitrogen trichloride production was about 0.4 mg/l (as N) when breakpoint effluent was used as the source of chlorine injector water. While the amount of chlorine consumed in its formation was relatively small (4 percent to 6 percent of total chlorine dosed), nitrogen trichloride generation affects the minimum ammonia concentration that can be achieved in breakpoint, since it decays slowly in dilute solution and it is converted to ammonia upon dechlorination with sulfite.

5. The concentration of organic nitrogen compounds was not affected by breakpoint chlorination.

6. The rate of reaction for breakpoint chlorination was found to vary depending upon the pH control point (final system pH), with fastest rates observed at a pH set point of pH 7.0. The time to completion was found to be between 60 sec and 90 sec at pH 7.0. The reaction rate slowed considerably at a pH set point of 6.5, and also became progressively slower as pH was increased from pH 7.3 to pH 8.5.

7. Variations in the amount of mechanical mixing intensity in the zone of breakpoint chemical application had no effect upon overall system chemical consumption and effluent quality. Mechanical mixing, to facilitate a rapid and thorough blending of process chemicals and influent stream, was important in damping oscillations in free chlorine concentration for control purposes.

8. Sodium hydroxide (NaOH) was used throughout the study as an alkalinity supplement. The amount required to neutralize all breakpoint acidity (1.53 lb NaOH/lb Cl_2) was essentially identical to that predicted from chemical stoichiometry.

9. In breakpoint chlorination systems which have gaseous chlorine as the chlorine source, the volume and chemical composition of the chlorine injector water may be important factors in process performance and control. At Rancho Cordova, when secondary effluent (breakpoint process influent) was used as the injector water source, more nitrogen trichloride formed in the injector water than when breakpoint effluent with low

ammonia content was used. Specific design recommendations for breakpoint chlorination chlorine injector water systems are given in the text.

10. The breakpoint chlorination control system recommended here, while comprised of commercially available components, can provide satisfactory nitrogen removal with minimum chlorine consumption only if it is tailored to the individual application. Specific recommendations for breakpoint process chlorine dosage control and pH control are made in the text.

SECTION 3

CHEMISTRY OF THE BREAKPOINT CHLORINATION PROCESS

The use of chlorine as a disinfectant in water treatment began in about 1800 in Europe. In about 1893, chlorine was applied as a wastewater disinfectant in New York. In the early 1920's, Houston[1] observed that high dosages of chlorine removed tastes and odors from water. The use of high dosages of chlorine in water treatment led some operators to observe the increase, disappearance and subsequent reappearance of chlorine residual as chlorine dosage was incrementally increased. These observations gave rise to the term "breakpoint" chlorination. Calvert[2] recognized in 1940 that the breakpoint phenomena was the result of the oxidation of ammonia nitrogen in solution.

This section presents the chemistry of chlorine and ammonia in aqueous solution, and describes the breakpoint reactions which can lead to oxidation of ammonia nitrogen to end products composed principally of nitrogen gas. Compounds of chlorine and of nitrogen may occur in a variety of species and proportions. For this reason quantitative terms herein are, unless otherwise noted, expressed in terms of the elemental forms, chlorine or nitrogen.

CHEMISTRY OF AMMONIA IN WATER

The actual chemical form of ammonia in dilute aqueous solution depends largely upon pH and temperature. The relative distribution of nondissociated ammonia and ammonium ion may be defined according to the equation below:

$$NH_4^+ \rightleftharpoons NH_3 + H^+ \qquad K = 5 \times 10^{-10} \text{ at } 20\ C \qquad (1)$$

where NH_3 = nondissociated ammonia

NH_4^+ = ammonium ion

H^+ = hydrogen ion

K = dissociation constant

According to the dissociation constant, the pH value at which nondissociated ammonia and ammonium ion are present in equal proportions (pK) is about pH 9.3 at 20 C. Above pH 9.3, nondissociated ammonia predominates. Below pH 9.3, ammonium ion predominates.

CHEMISTRY OF CHLORINE IN WATER

When chlorine gas is dissolved in water, a hydrolysis reaction occurs according to the following relationship:

$$Cl_2\ (GAS) + H_2O \rightleftharpoons HOCl + H^+ + Cl^- \qquad (2)$$

followed by a dissociation reaction:

$$HOCl \rightleftharpoons OCl^- + H^+ \qquad K = 3.3 \times 10^{-8} \text{ at } 20\ C \qquad (3)$$

where $HOCl$ = hypochlorous acid

OCl^- = hypochlorite ion

H^+ = hydrogen ion

K = dissociation constant

The pH value at which hypochlorous acid and hypochlorite ion are present in equal proportions (pK) is about 7.5 at 20 C. Above pH 7.5, hypochlorite ion predominates. Below pH 7.5, hypochlorous acid predominates. The total concentration of both hypochlorous acid and hypochlorite ion is commonly termed "free available chlorine."

Formation of Chloramines

When chlorine and ammonia are present in dilute aqueous solution, reactions can occur according to a number of chemical pathways. Reactions between chlorine and ammonia which result in the formation of chloramines are described below:

$$NH_4^+ + HOCl \longrightarrow NH_2Cl\ (\text{monochloramine}) + H_2O + H^+ \qquad (4)$$

$$NH_2Cl + HOCl \longrightarrow NHCl_2\ (\text{dichloramine}) + H_2O \qquad (5)$$

and

$$NHCl_2 + HOCl \longrightarrow NCl_3\ (\text{nitrogen trichloride}) + H_2O \qquad (6)$$

The relative amounts of the chloramine species which exist in solution depend upon certain process variables, including pH, temperature, contact time and the initial chlorine to ammonia

ratio (Cl_2:NH_4^+ -N). The total of the chloramine species present in solution is termed "combined" chlorine residual.

The ammonia nitrogen concentration of a wastewater effluent is typically in the range of 10 mg/l to 40 mg/l, unless an ammonia removal process such as biological nitrification has been employed. When chlorine is added to such an effluent for disinfection purposes (dosage of 2 mg/l to 15 mg/l), the predominant chlorine residual species in solution is ordinarily monochloramine (NH_2Cl).

The Breakpoint Reaction

Breakpoint chlorination occurs when sufficient chlorine has been added to a water or wastewater sample to cause the chemical oxidation of the ammonia in solution to nitrogen gas and other end products. Some disagreement still exists in the literature concerning the actual chemical pathway(s) for breakpoint chlorination, but the following set of reactions appear to be the most reasonable:

$$2NH_4^+ + 2HOCl \longrightarrow 2NH_2Cl + 2H_2O + 2H^+ \quad (4)$$

$$2NH_2Cl + 2HOCl \longrightarrow 2NHCl_2 + 2H_2O \quad (5)$$

$$NHCl_2 + H_2O \longrightarrow NOH + 2H^+ + 2Cl^- \quad (7)$$

$$NHCl_2 + NOH \longrightarrow N_2 + HOCl + H^+ + Cl^- \quad (8)$$

$$2NH_4^+ + 3HOCl \longrightarrow N_2 + 3H_2O + 5H^+ + 3Cl^- \quad (9)$$

where NOH = catalytic intermediary compound.

Combined with equation (2), the overall reaction is:

$$3Cl_2 + 2NH_4^+ \longrightarrow N_2 + 8H^+ + 6Cl^- \quad (10)$$

Note that breakpoint occurs through the sequential formation of monochloramine and dichloramine with the subsequent catalytic decomposition of dichloramine to end products of nitrogen gas, with a partial return of free residual (HOCl) to the solution. These reactions confirm that 1.5 moles (gram molecular weights) of chlorine are required to oxidize 1.0 mole of ammonia to nitrogen gas.

Stoichiometrically, the breakpoint reaction requires a weight ratio of chlorine to ammonia nitrogen (Cl_2:NH_4^+ -N) at the breakpoint of 7.6:1, as shown below:

Molecular weight Cl_2 = 70.9

Moles Cl_2 required = 1.5

Molecular weight NH_4^+ = 14.0 (expressed as N)

Moles NH_4^+ required = 1.0

Therefore, $Cl_2:NH_4^+$ -N = (1.5)(70.9):(1.0)(14.0) = 7.6:1.

The Breakpoint Curve

The breakpoint chlorination curve is a graphic representation of chemical relationships which exist as varying amounts of chlorine are added to dilute solutions of ammonia nitrogen. The theoretical breakpoint curve shown in Figure 3-1 has several characteristic features. The characteristics of the breakpoint curve shown in Zone 1 include principally the reaction between chlorine and ammonium indicated in Equation 4. The hump of the breakpoint curve occurs, theoretically, at a chlorine to ammonia nitrogen weight ratio of 5:1 (molar ratio of 1:1). That ratio corresponds to the point at which the reacting chlorine and ammonia molecules are present in solution in equal numbers.

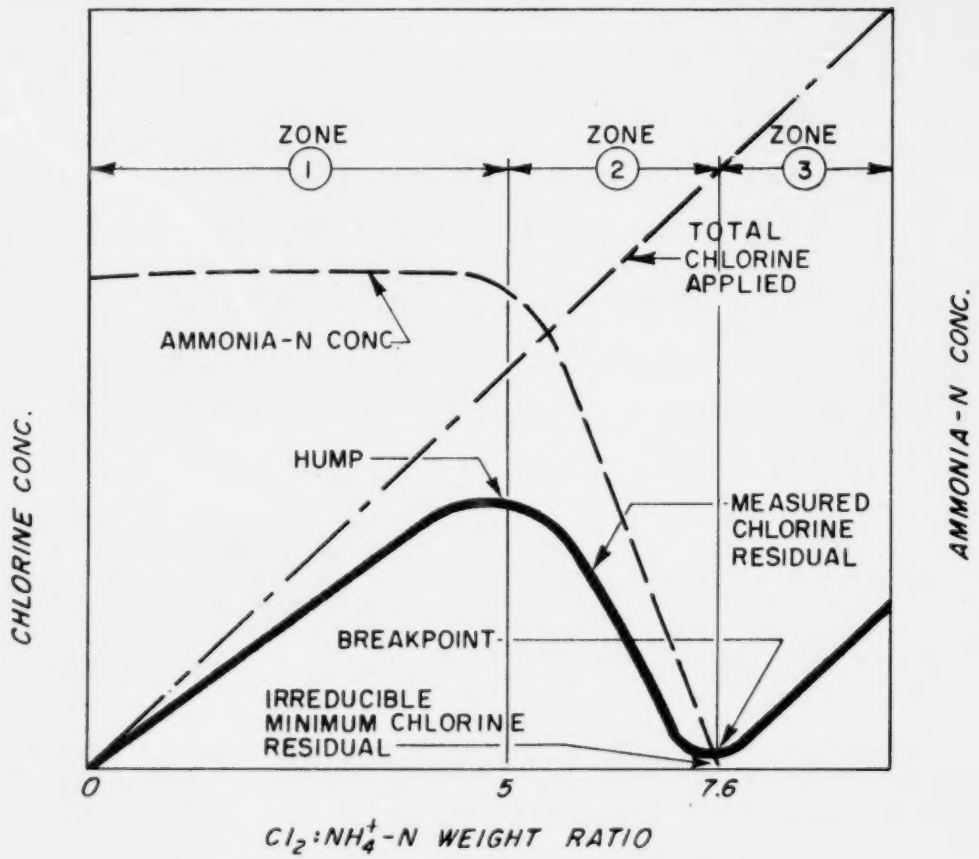


Figure 3-1 Theoretical Breakpoint Curve

The chemical equilibria of Zone 2 favor the formation of dichloramine and the oxidation of ammonium according to Equations 5, 7 and 8. These reactions proceed to, theoretically, a chlorine to ammonia nitrogen weight ratio of 7.6:1. At the breakpoint, the ammonium concentration is minimized.

To the right of breakpoint, Zone 3 chemical equilibria require the buildup of free chlorine residual.

In practical applications of breakpoint chlorination, reactions occur which result in the formation of nitrate, nitrogen trichloride and other end products. These reactions consume chlorine, cause the Cl_2:NH_4^+ -N ratio to exceed the theoretical value of 7.6:1 and affect the shape of the breakpoint curve. All of these observations are discussed in detail in subsequent sections of this report.

Other Reactions Encountered in Breakpoint Chlorination

Breakpoint chlorination of wastewater effluent can result in chemical reactions other than the direct oxidation of ammonia to nitrogen gas. Reaction products and chlorine consumption for such reactions are governed by factors such as the type and degree of pretreatment, initial chlorine to ammonia nitrogen ratio, pH and alkalinity. A summary of the common reactions encountered in breakpoint chlorination is given in Table 3-1.

Table 3-1. Common Reactions Encountered in Breakpoint Chlorination

Description	Reaction Stoichiometry	
"Breakpoint Reaction"	$2\ NH_4^+ + 3\ HOCl \rightarrow N_2 + 3\ H_2O + 5\ H^+ + 3\ Cl^-$	(9)
Nitrogen trichloride formation	$NH_4^+ + 3\ HOCl \rightarrow NCl_3 + 3\ H_2O + H^+$	(11)
Nitrate formation		
(1) from ammonia	$NH_4^+ + 4\ HOCl \rightarrow NO_3^- + H_2O + 6\ H^+ + 4\ Cl^-$	(12)
(2) from nitrite	$NO_2^- + HOCl \rightarrow NO_3^- + H^+ + Cl^-$	(13)
Reaction with other inorganics	inorganics + HOCl → oxidized inorganics	(14)
Chloro-organic reactions	organics + HOCl → oxidized organics	(15)

The total amount of chlorine residual consumed (by weight) for each of the common reactions encountered in breakpoint chlorination has been summarized in Table 3-2. For example, a total of 20.3 mg/l of chlorine residual (as Cl_2) is consumed in the conversion of 1.0 mg/l ammonia nitrogen to 1.0 mg/l nitrate (as N). A similar conversion from nitrite to nitrate requires only 5.1 mg/l chlorine.

Table 3-2. Chlorine Requirement for Chemical Transformations Commonly Encountered in Breakpoint Chlorination

Initial species	Reaction product	Cl_2:N molar ratio required	Cl_2:N weight ratio required
NH_4^+-N	N_2	1.5:1	7.6:1
NH_4^+-N	NCl_3	3:1	15.2:1
NH_4^+-N	NO_3^--N	4:1	20.3:1
NO_2^--N	NO_3^--N	1:1	5.1:1
Other inorganics	Oxidized inorganics	Varies	Varies
Organics	Oxidized organics	Varies	Varies

In effluents from biological secondary treatment processes, reduced inorganic compounds such as sulfides and ferrous iron have become oxidized by the aerobic treatment. Hence, reactions of inorganic compounds with chlorine are usually not quantitatively significant. Partially oxidized and slowly degradable organic matter is present, both in solution and in particulate suspended matter, which does react, particularly with free chlorine. Such matter includes nitrogen-containing proteinaceous matter.

pH AND ALKALINITY CONSIDERATIONS

The nature and concentration of the breakpoint chlorination end products, chlorine dosage required to reach breakpoint and the rate of the breakpoint reaction are all affected by the initial pH (following chemical addition) and the pH change which

occurs as the breakpoint reaction proceeds. The initial pH in the reaction zone and pH change through breakpoint depends upon the pH and alkalinity of the process influent stream, ammonia concentration and chlorine dosage, and the amount of alkalinity supplementation.

Acidity is generated in breakpoint chlorination applications from both the hydrolysis and dissociation of chlorine gas (when gaseous chlorine is used), and the oxidation of ammonia nitrogen as shown in Table 3-3. Stoichiometrically, three moles of hydrogen ions are liberated in the hydrolysis and dissociation of sufficient chlorine for the oxidation of one mole of ammonia nitrogen, assuming the initial pH in the reaction zone is alkaline. One mole of hydrogen ions is liberated in the oxidation of ammonia to nitrogen gas.

Table 3-3. Acidity and Alkalinity Considerations in Breakpoint Chlorination

Acidity source		
Hydrolysis and dissociation of chlorine	$3\ Cl_2 + 3\ H_2O \rightarrow 3\ OCl^- + \underline{6H^+} + 3Cl^-$	(16)
Oxidation of ammonia	$2\ NH_4^+ + 3\ OCl^- \rightarrow N_2 + 3\ H_2O + \underline{2H^+} + 3\ Cl^-$	(17)
Total	$3\ Cl_2 + 2\ NH_4^+ \rightarrow N_2 + \underline{8H^+} + 6\ Cl^-$	(10)
Alkalinity source		
Lime	$4\ CaO + 4H_2O \rightarrow 4Ca^{++} + 8\ \underline{OH^-}$	(18)
Sodium hydroxide	$8\ NaOH \rightarrow 8\ Na^+ + \underline{8\ OH^-}$	(19)

When an alkalinity source is added to neutralize breakpoint acidity, the acidity from chlorine hydrolysis and dissociation is neutralized immediately. The acidity from the oxidation of ammonia is released as the breakpoint reaction progresses. As a result, the pH in the breakpoint reaction chamber decreases as reaction time increases. At high initial ammonia concentrations and low system alkalinity, the pH excursion in the breakpoint reaction zone may be relatively large. Figure 3-2 shows a conceptual model for the range of pH values which would be encountered in breakpoint chlorination of 20 mg/l ammonia nitrogen in a secondary effluent with moderate pH buffer capacity.

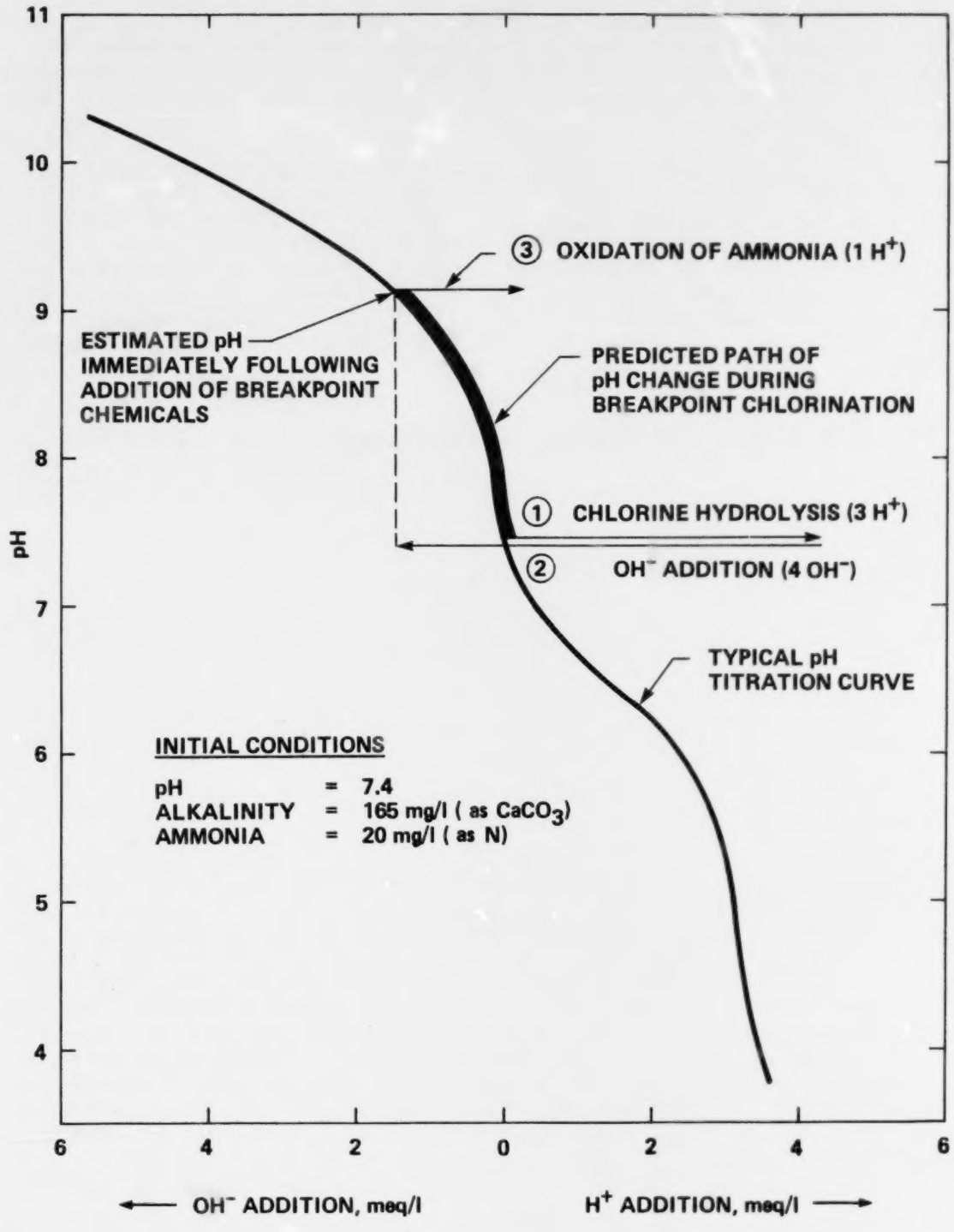


Figure 3-2 Conceptual Model for pH Change in Breakpoint Chlorination

SECTION 4

EXPERIMENTAL METHODS

The breakpoint chlorination demonstration program described here was carried out at the Rancho Cordova Wastewater Treatment Plant. The Rancho Cordova Plant, located in the Sacramento, California area, serves an area of 3,500 acres and a population of nearly 25,000. The average daily flow of about 2.4 mgd is composed primarily of domestic sewage. Secondary treatment is provided through primary sedimentation and a Spiro-Vortex activated sludge process. The secondary effluent is chlorinated for disinfection and discharged to the American River.

BREAKPOINT CHLORINATION FACILITIES

Breakpoint chlorination facilities were constructed at Rancho Cordova as indicated in the process schematic of Figure 4-1. A flow splitter box was constructed downstream of the secondary clarifier so that a predetermined fraction of the plant effluent could be passed through the breakpoint system. V-notch weirs in the splitter box were designed to pass 30 percent of the plant flow to the breakpoint system (Figure 4-2). That percentage was observed to be constant across the full range of plant flow rates. A capacitance probe, visible in Figure 4-2, was installed to sense liquid level upstream of the weir and electronic components were provided to perform flow computations.

Two existing chlorinators were used in the breakpoint study to control and meter the flow of chlorine to the breakpoint process. The chlorinators were 2,000 pound per day capacity Wallace and Tiernan variable V-notch devices. One was equipped with a 2,000 pound per day orifice and rotameter, the other had a 1,000 pound per day orifice and rotameter. Each had variable vacuum and automatic V-notch positioner controls. Chlorine gas was fed directly from ton cylinders, arranged in a dual manifold configuration with four cylinders per manifold. The automatic transfer system pictured in Figure 4-3 assured an uninterrupted flow of chlorine gas upon depletion of the cylinders on one manifold.

Sodium hydroxide was utilized throughout the study as an alkalinity supplement. It was purchased at 50 percent strength

and stored in a tank of approximately 8,000 gal. capacity. NaOH freezing problems encountered during cold weather were solved by insulation of the storage tank and heating of exposed caustic feed piping. A Wallace and Tiernan variable speed chemial feed pump, equipped with an SCR drive, was used to provide the required dosages of sodium hydroxide to the breakpoint system.

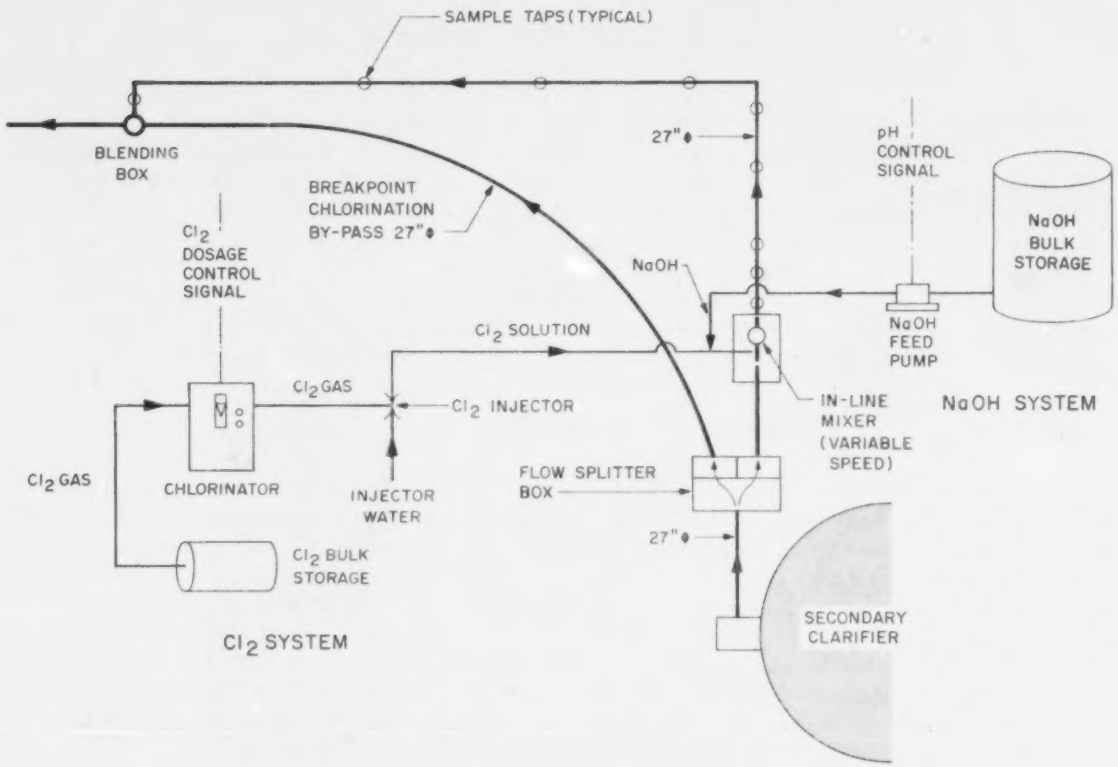


Figure 4-1 Process Flow Schematic

The 50 percent sodium hydroxide stream was added to the chlorine injector water immediately upstream of the chlorine application point, as shown in Figure 4-4. The chemicals were introduced into the process flow through a 4-inch diameter PVC injector pipe which extended across the 27-inch diameter influent pipe from the crown to the invert. Three-eighths inch diameter orifices were spaced along the injector pipe to allow a uniform application of the 100 gpm chlorine-sodium hydroxide chemical solution to the process influent stream. The orifices provided a head-loss of about 10 feet which assured near-equal distribution of the chemical solution across the influent pipe cross-section and provided an increment of initial mixing energy.

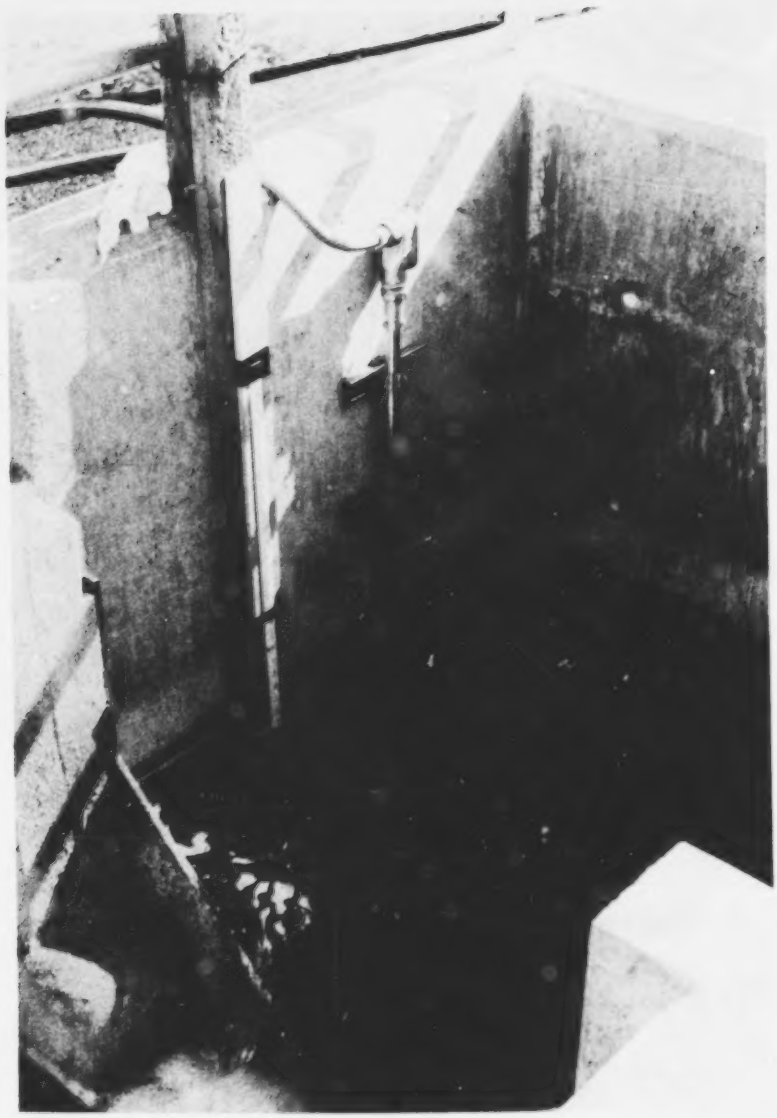


Figure 4-2 Flow Splitter Box

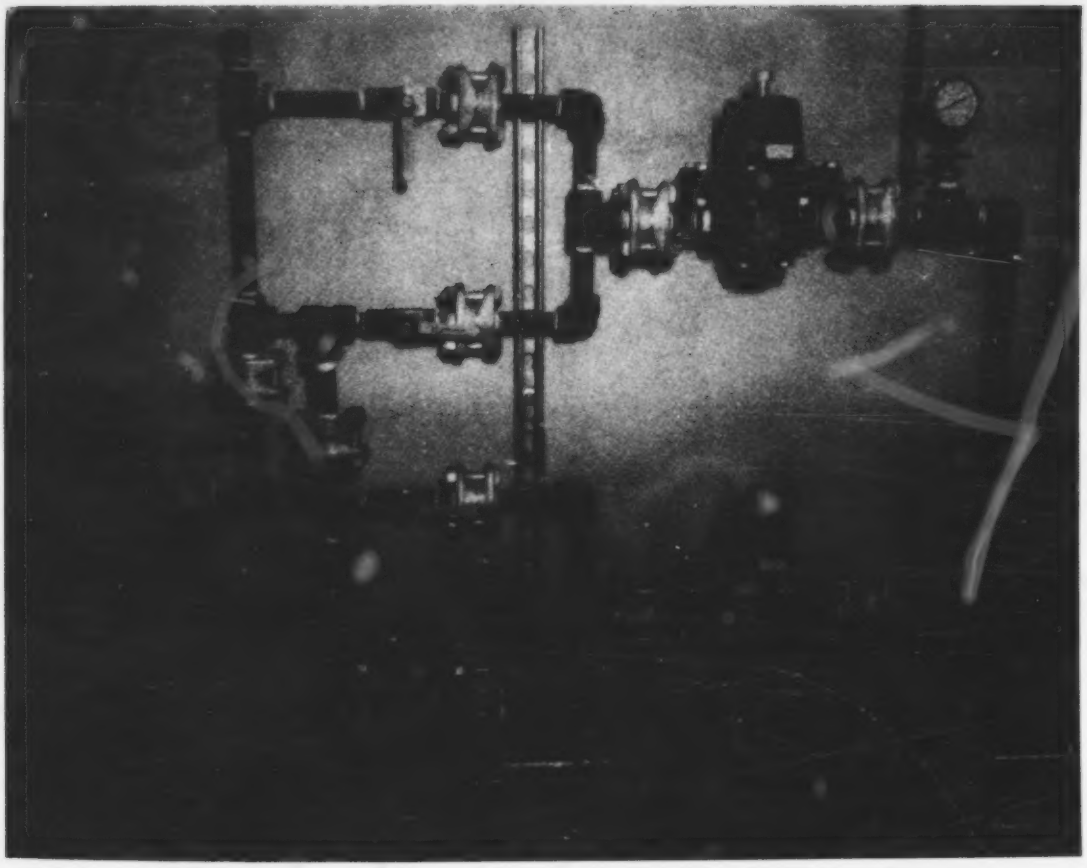


Figure 4-3 Automatic Chlorine Transfer Piping

A 3 hp variable speed mixing device (Figure 4-4) was installed in the process stream immediately downstream of the chemical application point. Two mixer propellers installed on the mixer shaft were capable of delivering mixing intensity, as measured by the mean velocity gradient (G), of up to 1,500 to 2,000 sec^{-1} in the chemical addition zone.

Eight sample taps (extending to the center of the break-point process pipeline) and two sampling pumps allowed selective withdrawal of samples from the process pipe. The exact contact period could be determined for each of the samples collected by means of the sampling system. A photo of the sampling system is given in Figure 4-5.

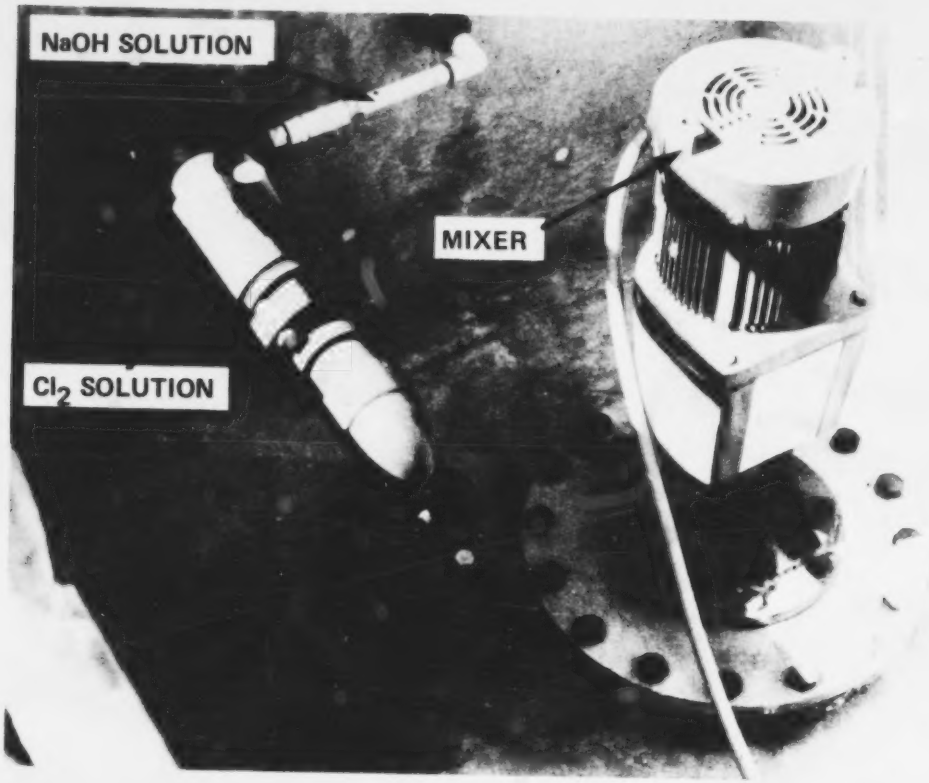


Figure 4-4 Chlorine and NaOH Application Point

A sulfur dioxide (SO_2) dechlorination system was installed to provide emergency dechlorination for the Rancho Cordova plant effluent when measured effluent chlorine residuals exceeded tolerable levels. Breakpoint process control was maintained throughout the study so that emergency dechlorination was required on very few occasions.

CONTROL AND MONITORING EQUIPMENT

Several important primary elements in the overall process control and monitoring system are discussed below. Design considerations which can contribute to the successful operation of each of the elements in the control system are given in Section 6, Process Control.

Free Chlorine Residual Analyzer

The free chlorine residual analyzer used throughout the breakpoint program was a Fischer and Porter "Anachlor" unit. A small chemical feed pump provided a continuous feed of pH buffer

and bromide to the measuring cell. The flow of sample from the constant head tank to the measuring cell was controlled by a needle valve. Free chlorine residual was determined amperometrically from the amount of bromide converted to bromine under acidic conditions in the measuring cell.

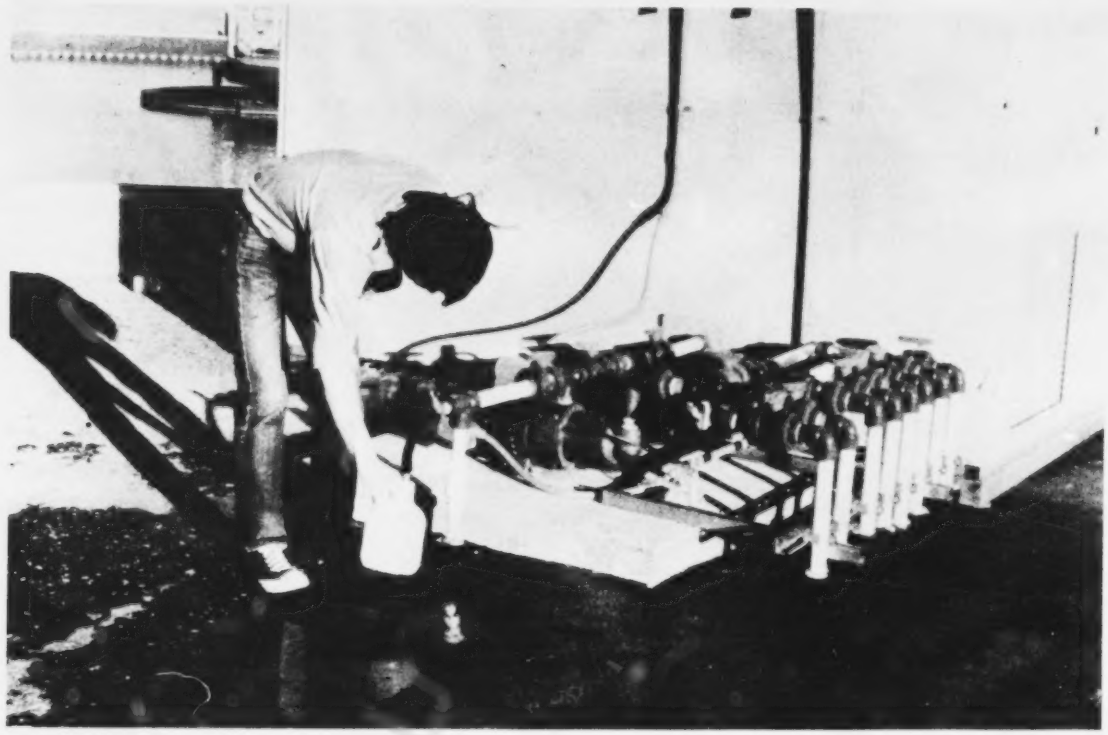


Figure 4-5 Sampling System

Ammonia Nitrogen Analyzer

The concentration of ammonia nitrogen in the process influent was analyzed continuously using an automatic analyzer, Technicon Type I. An alkaline phenate colorimetric procedure was used.

pH Monitor

A continuous analysis of breakpoint effluent pH was maintained using a Leeds and Northrup system.

LABORATORY TESTING PROCEDURES

Chemical and physical analyses were performed according to Standard Methods for the Examination of Water and Wastewater[3] 14th edition, except as noted below for specific analyses.

Ammonia Nitrogen (NH_3 -N)

The ammonia nitrogen determinations performed on-site were made using a commercial ammonia nitrogen probe (Orion Research, Inc., Model 95-10) combined with a pH-specific ion meter (Leeds and Northrup Model 7417). The probe was calibrated daily using ammonium chloride standard solutions.

Samples collected and preserved for subsequent testing of ammonia nitrogen at a commercial laboratory were analyzed, using distillation and titration procedures for ammonia levels greater than 1 mg/l, and by distillation and nesslerization at ammonia concentrations below 1 mg/l.

Nitrate Nitrogen (NO_3^- -N)

Nitrate analyses were performed according to brucine procedures, except for chlorine injector water samples which interfered with the brucine analysis. Injector water samples were analyzed using cadmium reduction techniques.

Chlorine Species

Both free and combined chlorine residual species were analyzed routinely throughout the breakpoint study using a Wallace and Tiernan Amperometric Titrater. Iodometric techniques were used to measure the high chlorine residuals found in samples of the chlorine injector water.

SECTION 5

RESULTS AND DISCUSSION

Breakpoint chlorination testing was carried out at Rancho Cordova, California, during a three-month period, from mid-December, 1975 through March 15, 1976. Test data were collected to provide insights into process chemistry and control. The system was operated continuously, 24 hours per day, 5 days per week. Technicians were present at all times to collect operating data and adjust the system as needed. Specific results of the breakpoint chlorination testing program are presented and discussed below and presented in Appendix A. Additional data from continuous recording devices, too bulky for inclusion in this report, are retained on file by the engineers.

PROCESS INFLUENT CHARACTERISTICS

The breakpoint chlorination system at Rancho Cordova functioned on-line, with full effluent flow and chemical quality variations. Diurnal variations in flow caused breakpoint process flow rates to vary from about 0.1 mgd to 1.2 mgd. Ammonia nitrogen concentrations were also observed to vary on a diurnal basis over a range of about 15 mg/l to 25 mg/l. Ammonia mass flow, the product of process flow and ammonia concentration, was found to vary on a typical day according to the plot of Figure 5-1. As therein indicated, the ratio of ammonia mass rate maximum to minimum was typically about 8 to 1.

Rancho Cordova Wastewater Treatment Plant effluent is a high quality secondary effluent, as evidenced by the data summarized in Table 5-1. The concentrations of nitrogen species and the average alkalinity of 165 mg/l are typical of non-nitrified secondary effluent.

INITIAL MIXING

A series of tests were conducted in which the mechanical mixing intensity at the point of chemical application was varied and effects upon process performance were monitored. None of the observations showed any effect upon chemical consumption or effluent quality as the mechanical mixing intensity was increased from zero (mixer turned off) to the maximum (G = 1500

to 2000 sec^{-1}) level attainable. With the mechanical mixer off, the free residual analyzer sensed somewhat greater variations in free chlorine residual as compared to that with the mixer on full speed; however, the mid-point in the oscillation was the same in both cases. While the increased amplitude of the free chlorine residual excursions did not affect chemical consumption or effluent quality, process control functions were made more complicated and, for this reason, mechanical mixing was employed throughout the study.

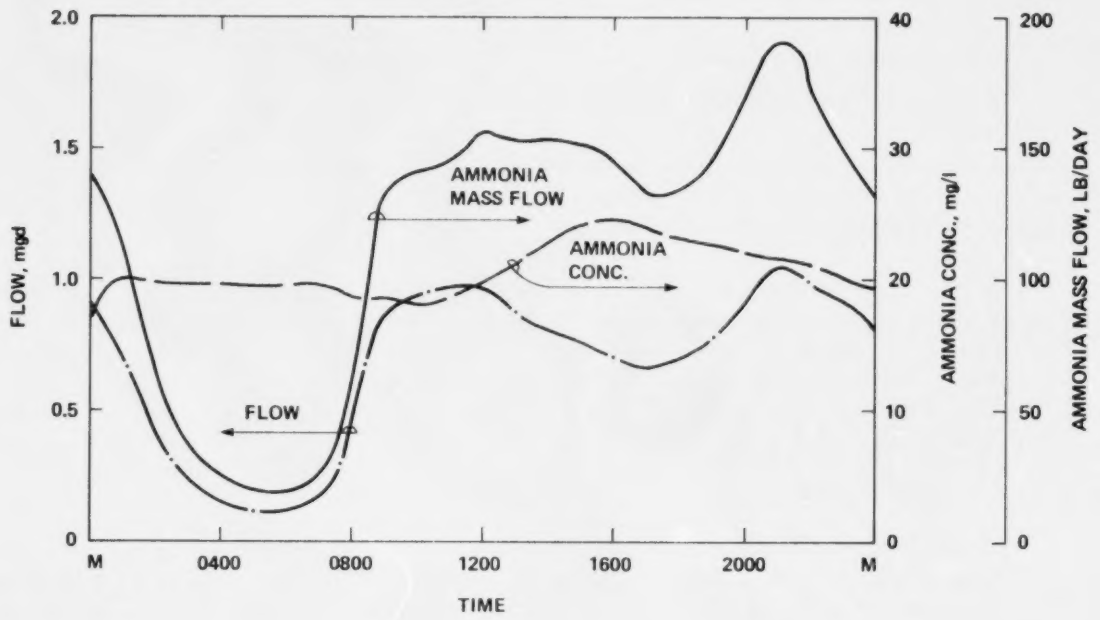


Figure 5-1 Process Influent Variations

From the Rancho Cordova data, the total dosage of chlorine necessary to reach breakpoint is not measurably affected by the intensity of initial mixing. However, process control considerations dictate that segregation of the reactants be minimized. For design purposes, sufficient hydraulic or mechanical energy should be provided to facilitate rapid and thorough blending of the chlorine solution, pH adjustment chemical and process influent. Rapid mix design criteria from water treatment practice should serve as a design guideline.

Table 5-1. Secondary Effluent Quality, Rancho Cordova, California

Parameter	Average value	Range
BOD	8 mg/l	6-10 mg/l
COD	32 mg/l	11-45 mg/l
pH	7.2	7.0-7.4
Alkalinity (as $CaCO_3$)	165 mg/l	150-175 mg/l
NH_4^+ (as N)	20.6 mg/l	15-25 mg/l
NO_2^- (as N)	0.6 mg/l	0.01-1.4 mg/l
NO_3^- (as N)	0.8 mg/l	0.07-1.4 mg/l
Total organic nitrogen (as N)	2.4 mg/l	1-5 mg/l
Soluble organic nitrogen (as N)	1.2 mg/l	1-2 mg/l
Turbidity	4 JTU	2-10 JTU

REACTION RATES

The time required for the breakpoint reactions to reduce to a minimum the ammonia nitrogen in solution depends upon the initial concentration of ammonia, chlorine dosage, pH, alkalinity and temperature. The consistent chemical quality of the Rancho Cordova effluent did not permit testing of all process variables across a wide range of conditions. Test data were collected which clearly documented the effect of pH set point (final system pH) upon the rate of reaction.

Figures 5-2 through 5-9 present breakpoint chlorination reaction rate data collected at Rancho Cordova for final pH values between pH 6.5 and pH 8.5. For each test, the control system was set to provide a free residual chlorine concentration in the process effluent of 12 mg/l. This was done to ensure sufficient chlorine residual in the combined breakpoint and nonbreakpoint stream to facilitate adequate disinfection of the plant effluent. Influent ammonia nitrogen concentrations exceeded 15 mg/l except in two test periods (pH set point 7.3 and 7.7) when the breakpoint effluent used as injector water diluted the influent ammonia concentration at low flows to concentrations of about 9 mg/l to 15 mg/l. The implications of the chlorine injector water source are discussed in a subsequent section of this report.

The reaction rate data are summarized in Table 5-2. The rate of the breakpoint reaction was observed to be fastest at a pH set point (final pH) of 7.0. The reaction rate slowed considerably at pH set point 6.5, with gradual reductions in rate observed across a range of pH set points from pH 7.3 to 8.5.

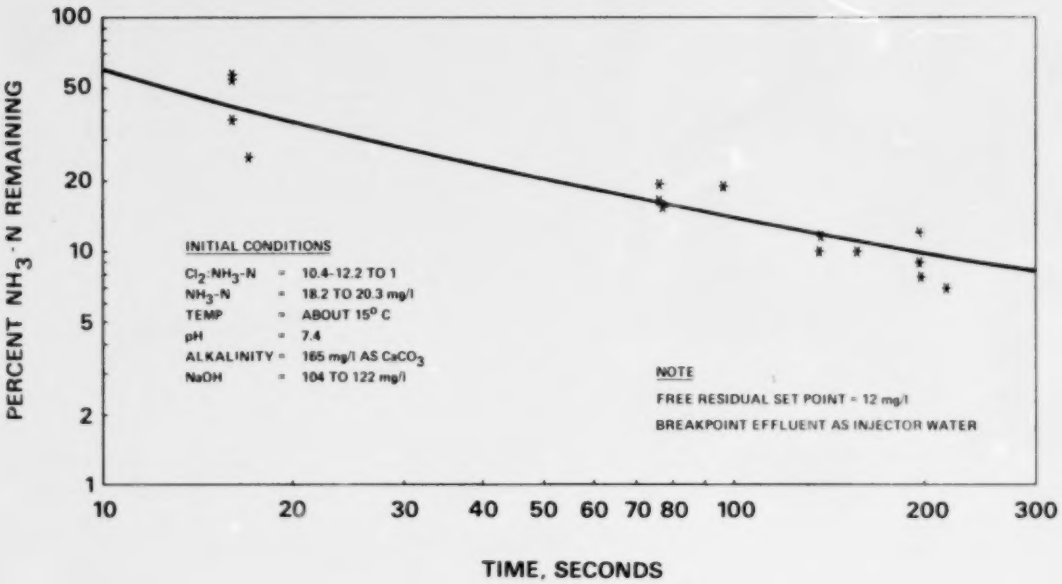


Figure 5-2 Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor - pH Set Point 6.5

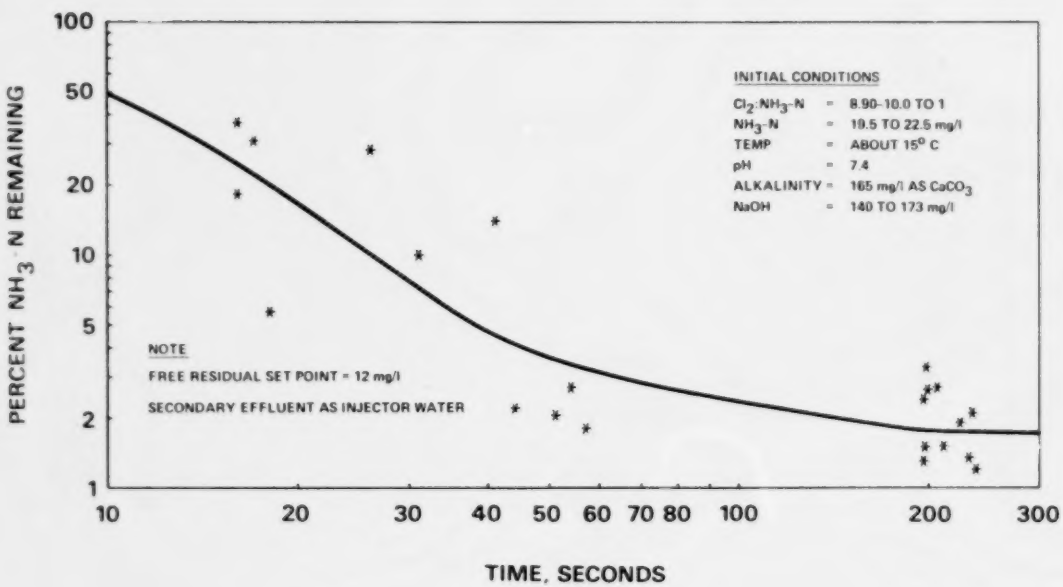


Figure 5-3 Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor - pH set Point 7.0

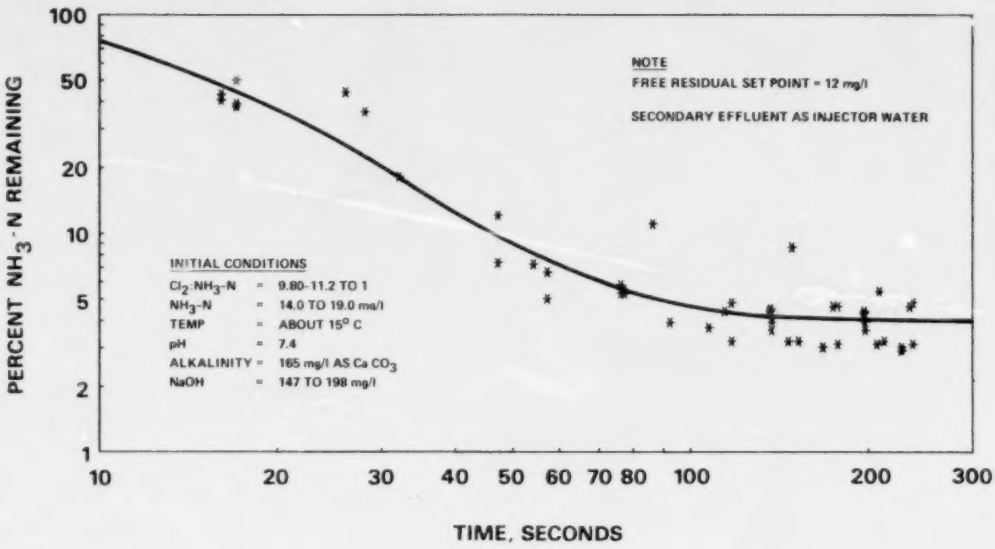


Figure 5-4 Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor - pH Set Point 7.0

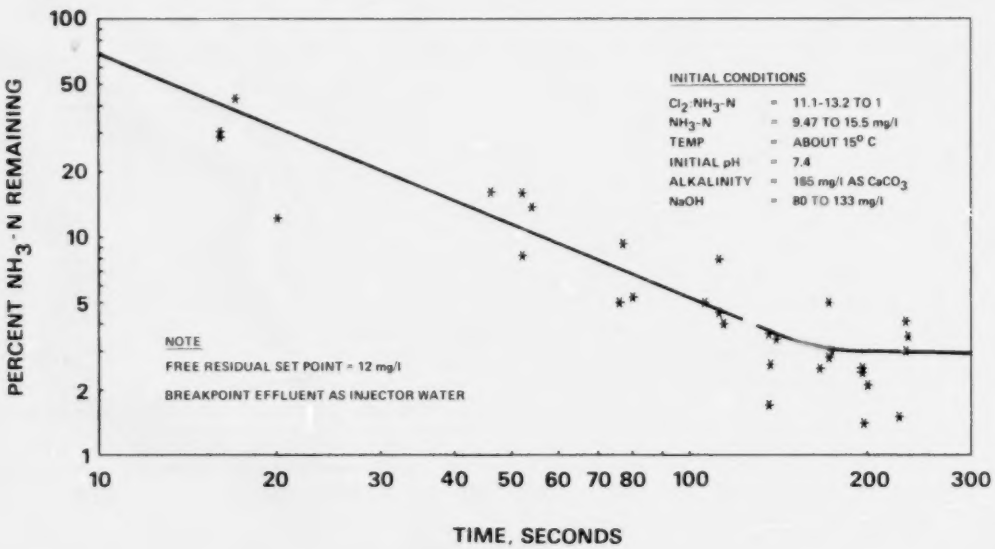


Figure 5-5 Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor - pH Set Point 7.3

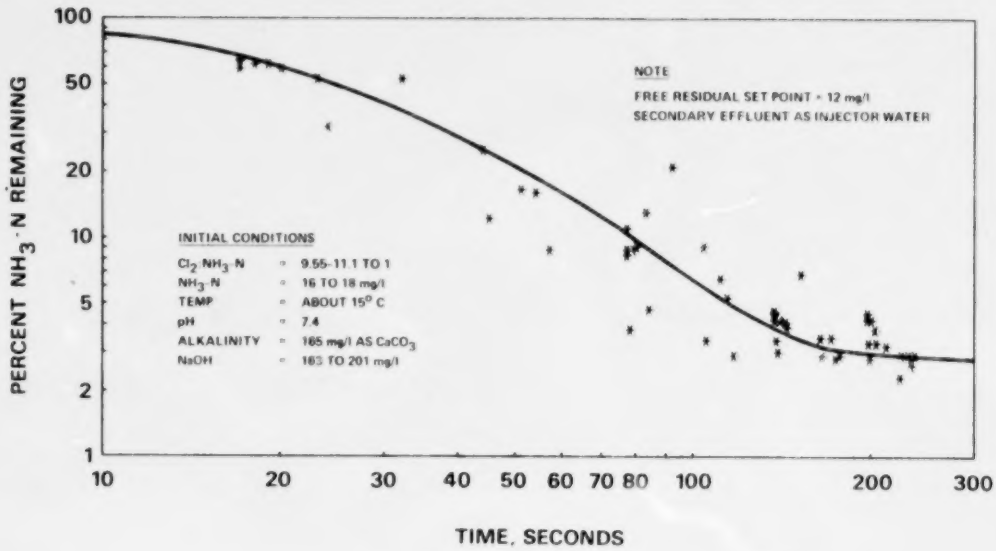


Figure 5-6 Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor - pH Set Point 7.5

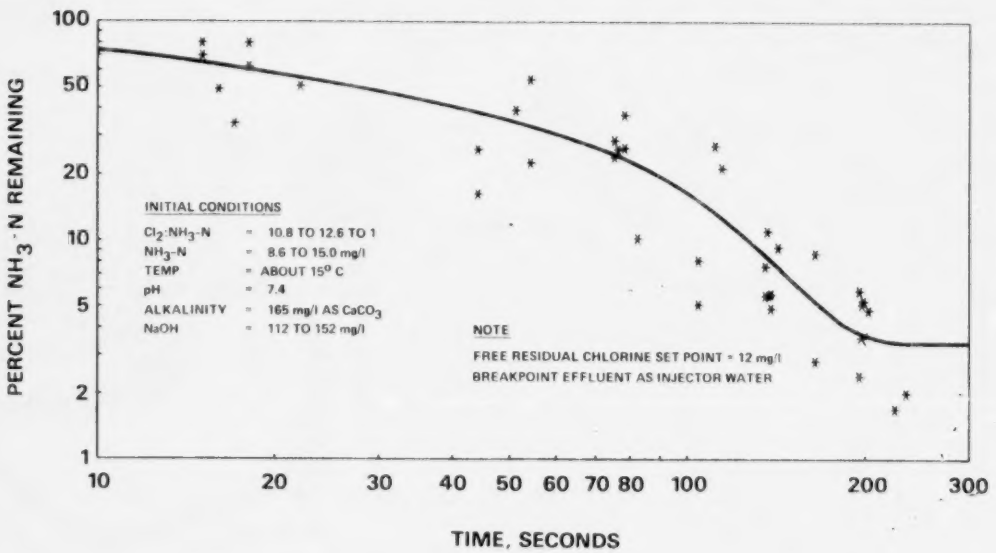


Figure 5-7 Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor - pH Set Point 7.7

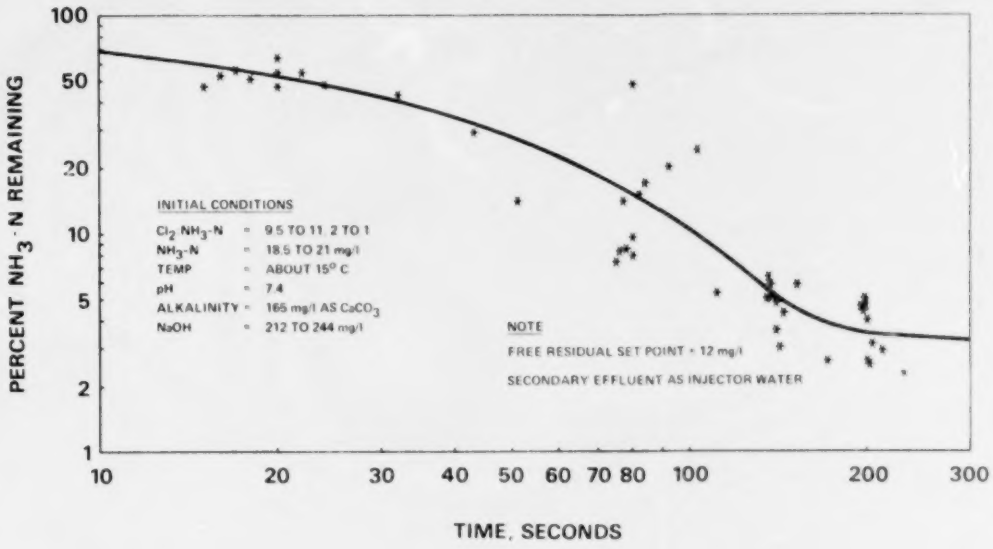


Figure 5-8 Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor - pH Set Point 8.0

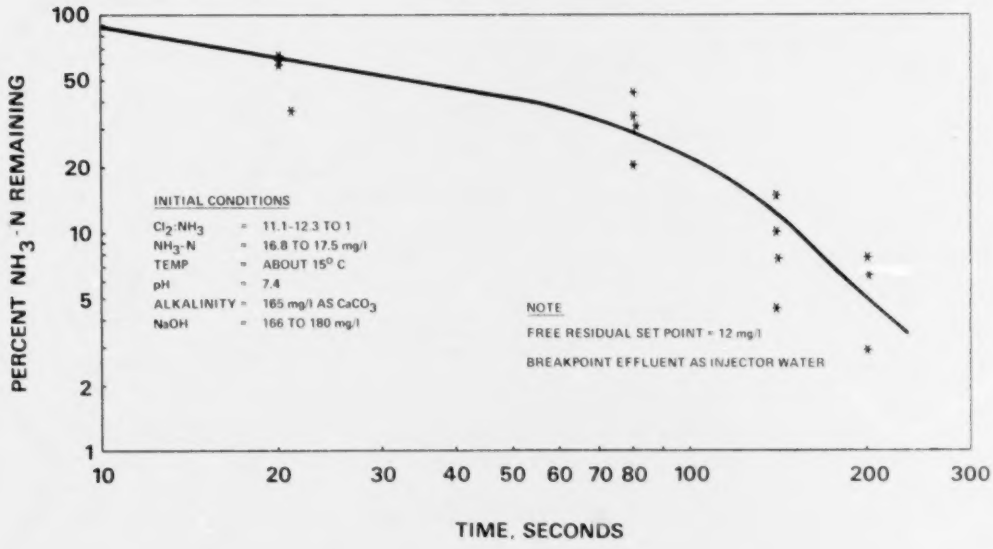


Figure 5-9 Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor - pH Set Point 8.5

Table 5-2. Reaction Rate Data Summary

pH set point	Injector water source[1]	Influent NH_4^+-N conc.	Estimated time to completion of breakpoint reaction
6.5	BP	18.2-20.3 mg/l	> 200 sec
7.0	SE	19.5-22.5 mg/l	60 sec
7.0	SE	14-19 mg/l	90 sec
7.3	BP	9.5-15.5 mg/l	130 sec
7.5	SE	16-18 mg/l	150 sec
7.7	BP	8.6-15 mg/l	180 sec
8.0	SE	18.5-21 mg/l	200 sec
8.5	BP	16.8-17.5 mg/l	> 200 sec

[1] BP = breakpoint effluent
SE = secondary effluent

NITROGENOUS RESIDUALS

Nitrogenous residuals formed in breakpoint chlorination include both nitrogen trichloride (NCl_3) and nitrate (NO_3^-). Nitrogen trichloride may be formed according to Equation 6, although Saunier, et al.[4] noted that reaction kinetics suggested that formation occurred through a more complex chemical pathway. Nitrate is formed in breakpoint chlorination through the oxidation of nitrite (NO_2^-) according to Equation 13, or by oxidation of ammonia as shown in Equation 12 (see Table 3-1). Formation of nitrogen trichloride or nitrate is undesirable, since large quantities of chlorine may be consumed, nitrogenous residuals persist in solution which reduce the nitrogen removal capability of the process, and obnoxious odors can result.

Nitrogen Trichloride

The residual ammonia concentration achieved following breakpoint chlorination was shown by Saunier, et al.[4] to be a function of nitrogen trichloride formation, since NCl_3 is converted to ammonia upon dechlorination with sulfite. Nitrogen trichloride is formed in breakpoint chlorination and, since it has a relatively slow decay rate, the amount formed serves to limit the degree of ammonia removal which can be attained in breakpoint chlorination.

The amount of "apparent" ammonia nitrogen remaining in solution (see Table 5-3) following breakpoint chlorination was assumed in this study to be a measure of the amount of nitrogen trichloride in solution. Nitrogen trichloride formation did not appear to be sensitive to the pH set point (final pH), with values generally observed to be in the range of 0.3 mg/l to 0.7 mg/l. This is contrary to the observations of Pressley, et al.[5] and Wei[6] who noted a strong pH dependency for nitrogen trichloride production. In a recent study by Saunier[4] some pH dependency was noted, but not to the degree reported by Pressley, et al., and Wei.

Table 5-3. Formation of Nitrogen Trichloride and Nitrate

pH set point	Injector water source[a]	NCl_3 formed, mg/l as N		NO_3^- formed[c], mg/l as N	
		Mean	Standard deviation	Mean	Standard deviation
6.5	BP	-	-	0.95	0.18
7.0	SE	0.43	0.15	-	-
7.0	SE	0.65	0.14	1.14	0.17
7.3	BP	0.34	0.12	0.93	0.27
7.5	SE	0.57	0.13	1.18	0.14
7.7	BP	0.52	0.27	1.19	0.31
8.0	SE	0.73	0.22	0.78	0.19
8.5	BP	-[b]	-[b]	1.25[d]	-

[a] BP = breakpoint effluent.
SE = secondary effluent.

[b] Reaction had not progressed to completion in samples collected.

[c] This category includes NO_3^- formed from NH_4^+, does not include NO_3^- formed from NO_2^-.

[d] One data point.

A careful analysis of the nitrogen trichloride data showed that the chlorine injector water source influenced the amount produced in the Rancho Cordova breakpoint system. A detailed discussion of the effect of injector water on that formation is given in a subsequent section of this report.

One possible explanation for the apparent discrepancy in observations on nitrogen trichloride production is that the choice of sampling and analysis procedures may be important in the results obtained. Nitrogen trichloride is known to be soluble to a very limited degree in water. Its characteristically pungent odor was noticeable at times in the sample building at Rancho Cordova. However, any which escaped from the breakpoint process in a gaseous form was not accounted for in any of the analytical measurements. Loss in gaseous form could

have occurred inside the breakpoint contact pipe. Nitrogen gas from the breakpont reaction may have stripped nitrogen trichloride from solution as it precipitated from solution and migrated, as bubbles, toward the top of the pipe. The milky appearance of samples pumped from the breakpoint system attested to the presence of gas bubbles in the breakpoint stream. Also, NCl_3 could have escaped from solution as the samples were being taken at the sample tap. In any case, it is possible that gaseous losses of NCl_3 in the Rancho Cordova system contributed to the apparent discrepancy in observations on NCl_3 formation vs system pH.

Another potential source of disagreement in NCl_3 observations is that different analytical techniques give different degrees of accuracy and precision. The DPD-FAS method was observed by Pressley, et al.[5] to have poor reproducibility, whereas the spectrophotometric method employed in the Blue Plains work was of questionable accuracy due to the carbon tetrachloride extraction and potential for interferences.

The amount of chlorine residual consumed in the oxidation of NH_4^+ to NCl_3 was found to be about 4 to 6 percent of the total chlorine dose across a pH range of pH 7 to 8. A complete data summary of the chlorine consumption of the chemical reactions encountered in breakpoint chlorination is given in Appendix A.

From the NCl_3 data and other qualitative observations made at Rancho Cordova, it appears that breakpoint systems may be designed without any provision for off-gas collection and treatment (for NCl_3 odors) if proper attention is given to the design of chlorine dosage and pH control systems. A complete discussion of factors to consider in the design of breakpoint process control is given in Section 6.

Nitrate

Data on NO_3^- formation in the Rancho Cordova breakpoint system are summarized in Table 5-3. It should be noted, however, that the data of Table 5-3 show the concentration of NO_3^- formed from NH_4^+, and do not include that formed from NO_2^-. Highly variable NO_2^- concentrations in the breakpoint influent stream tended to obscure the rather consistent pattern of NO_3^- formation which was observed to occur through the chemical pathway from NH_4^+. A more complete presentation of NO_3^- data is in Appendix A.

Nitrate formation was not observed to be pH dependent in this study. This is consistent with the experimental observations and breakpoint mathematical model predictions of Saunier[4], but it does not agree with the findings of Pressley, et al.[5]

The amount of chlorine consumed in the formation of NO_3^- from NH_4^+ was significant, varying from about 8 percent to 19 percent of the total chlorine dosage. As such, it represented the second largest chlorine consumption of the chemical reactions identified during the study.

Organic Nitrogen

Analysis of data collected to determine the effect of breakpoint chlorination on organic nitrogen compounds showed little change in organic nitrogen concentrations through the process. A statistical summary of total organic nitrogen data is given in Figure 5-10.

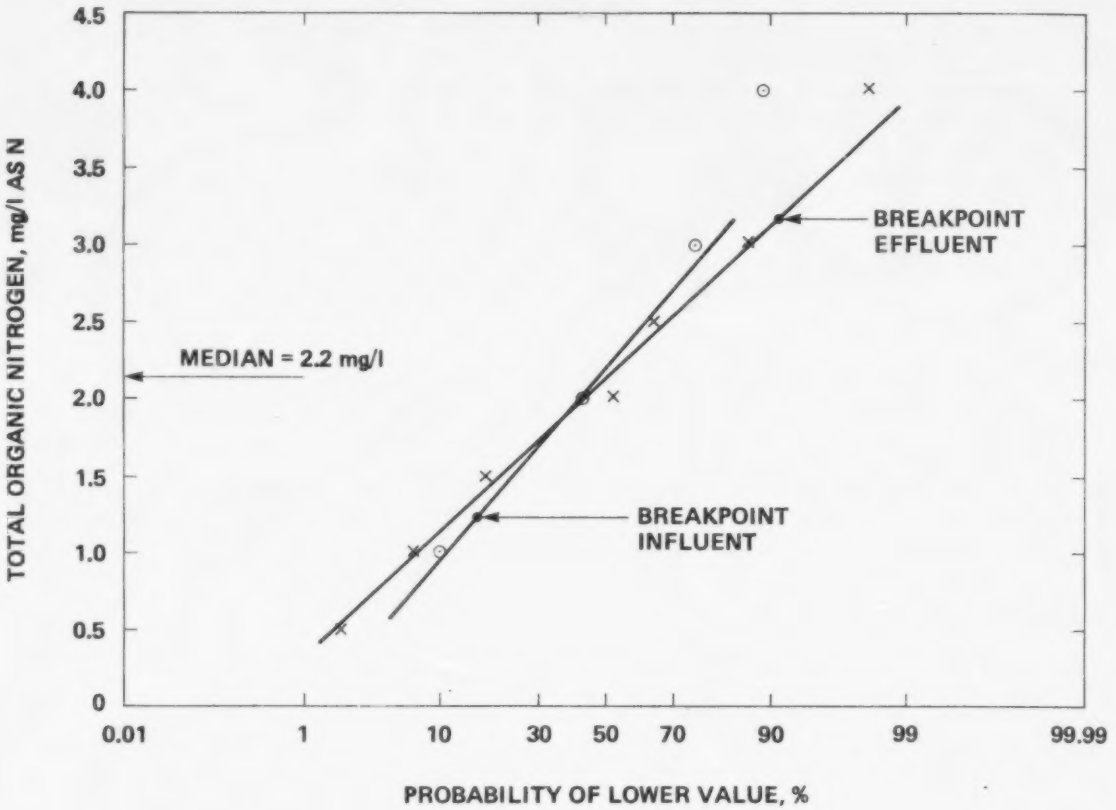


Figure 5-10 Effect of Breakpoint Chlorination on Organic Nitrogen

OVERALL CHLORINE CONSUMPTION

The total chlorine dosage necessary to maintain breakpoint chlorination at Rancho Cordova averaged 10.0 mg/l chlorine for each 1.0 mg/l of influent ammonia nitrogen (Cl_2:NH_4^+ -N = 10:1).

The statistical distribution of Cl_2:NH_4^+ -N values observed at Rancho Cordova is presented in Figure 5-11. This value may be compared to that predicted by the stoichiometry of the breakpoint reaction (Equation 9), which predicts only 7.6 mg/l chlorine consumed for each 1.0 mg/l ammonia. The difference in chlorine consumption between the theoretical and actual value may be attributed largely to other chemical reactions (Equations 11-12) which occur between chlorine and ammonia to form nitrate (NO_3^-) and nitrogen trichloride (NCl_3^-), as well as the free chlorine residual remaining in solution. A presentation of Rancho Cordova data showing the proportionate chlorine demand for each of the breakpoint reactions is given in Figure 5-12.

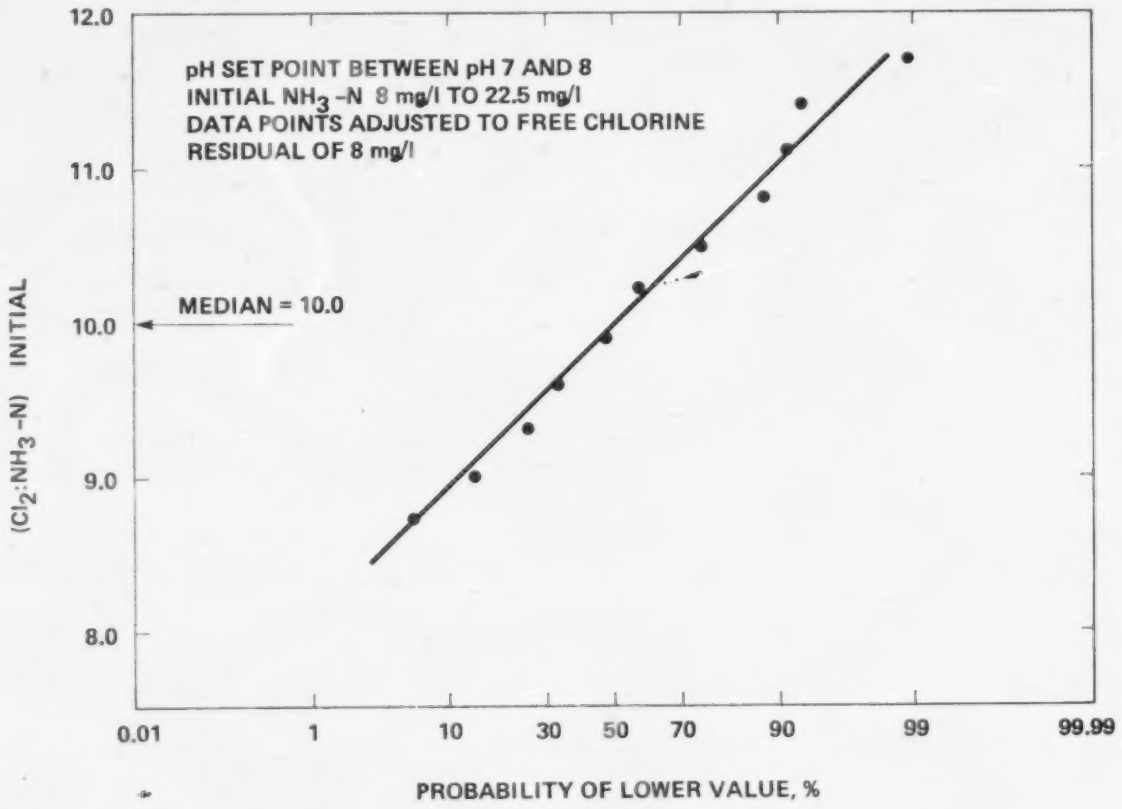


Figure 5-11 Summary of Cl_2: NH_4^+-N Observations

ALKALINITY SUPPLEMENTATION

An analysis of the quantity of sodium hydroxide fed to the breakpoint system for purposes of pH control showed that an average of 1.53 lb NaOH were added for each 1.0 lb chlorine to maintain the breakpoint system pH between pH 7.0 and 7.5. The

statistical distribution on the NaOH dosage data is presented in Figure 5-13. The value of 1.53 lb NaOH/lb Cl_2 compares favorably with the 1.50 lb NaOH/lb Cl_2 requirement predicted from stoichiometry (Equation 19). It should be noted that if lime (CaO) were used for pH control, chemical stoichiometry (Equation 18) predicts a requirement of 1.05 lb CaO/lb Cl_2.

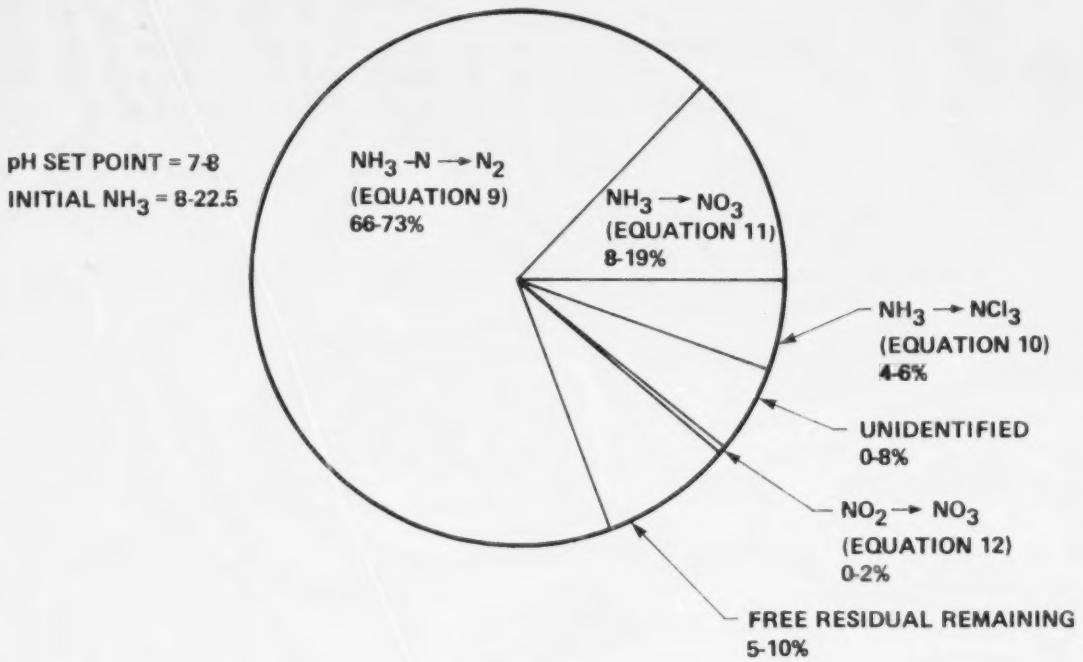


Figure 5-12 Breakpoint Chlorination Chlorine Consumption

CHLORINE INJECTOR WATER CONSIDERATIONS

When chlorine gas is used as the chlorine source in breakpoint chlorination, the volume and source (chemical composition) of the injector water may become important in process operation. Ordinary chlorine injector design criteria restricts the chlorine concentration in the injector water to 3,500 mg/l or less under maximum feed conditions. As a result, the high chlorine application rates in breakpoint chlorination can cause the injector water flow to be a significant fraction of the total process stream at low breakpoint process flow rates. If breakpoint process influent is used as injector water, reactions between chlorine and ammonia which occur in the injector water can consume chlorine in undesirable side reactions. If breakpoint process effluent is used as injector water, the reacting

constituents are diluted and reaction rates reduced, though the reduction would not be noticeable in most cases.

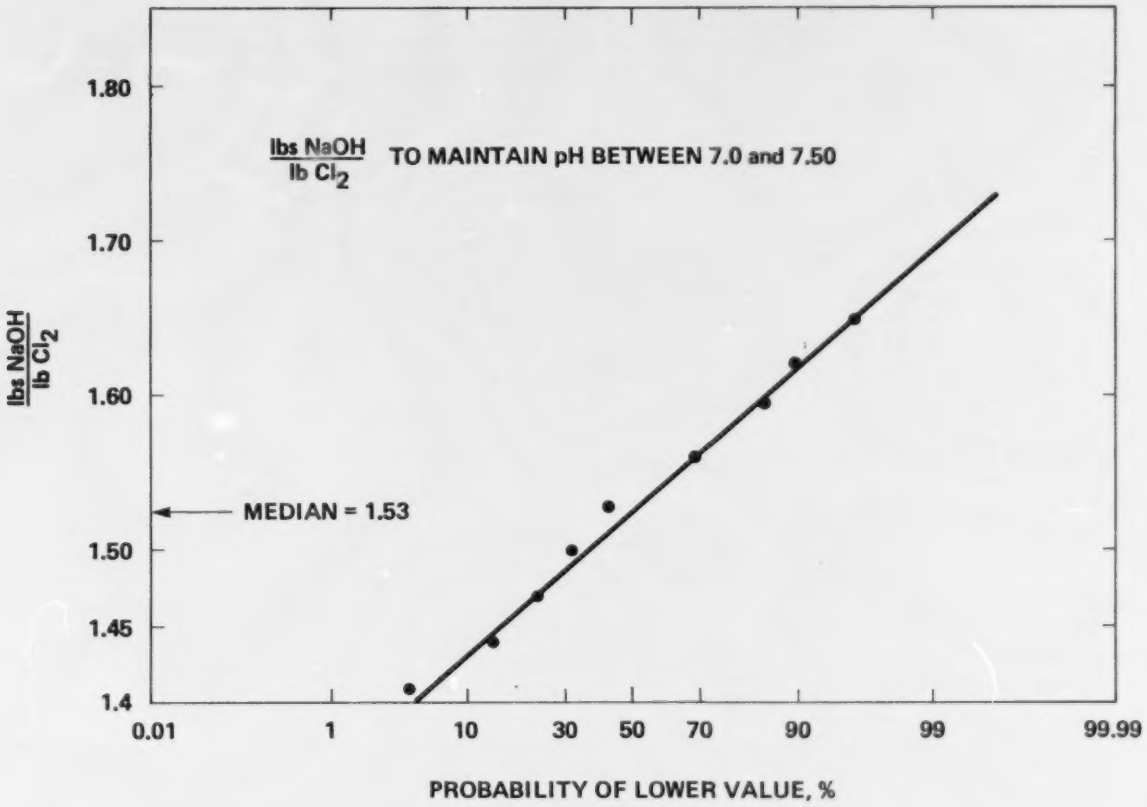


Figure 5-13 Lb NaOH/Lb Cl_2 Added

An analysis of Rancho Cordova data collected at pH set points between 7.0 and 8.0 showed that approximately 0.2 mg/l more NCl_3 was present in the process stream when secondary effluent (breakpoint influent) was used as injector water than when breakpoint effluent was used for chlorine injection. Contact time in the injector system was about 20 sec.

Samples of injector water were collected just prior to and following NaOH additions. Some of the samples were vigorously agitated during collection in an effort to drive off any NCl_3 which had formed, so that the amount of NCl_3 formed in the chlorine injector water could be estimated. The sampling techniques and analysis of injector water samples confirmed that NCl_3 was formed in significant amounts in the secondary effluent used as injector water. Nitrate concentrations in the injector water were not appreciably increased.

Based upon the Rancho Cordova testing, chlorine injector water in breakpoint chlorination applications should be designed according to the following criteria:

- If possible, locate the chlorine injector at the chemical application point and use process influent as injector water.

- If the injector must be remote from the actual application point, use process effluent as injector water.

- In large installations, it may be preferable to feed liquid chlorine (rather than gaseous), mixed with the alkalinity supplement chemical and sufficient process effluent to yield a maximum chlorine residual in the feed stream of 8,000 mg/l.

BREAKPOINT MODEL PREDICTIONS

As a supplementary part of this study, the breakpoint chlorination computer model developed at the University of California by Saunier and Selleck[4] was used to predict process performance under a variety of conditions, including many which could not have been tested under actual field conditions at Rancho Cordova. Those predictions are given in Appendix B of this report.

Figures B-1 through B-8 represent breakpoint model predictions under the exact conditions of the field-scale measurements presented in Figures 5-2 through 5-9. As such, the curves can be compared directly to determine the correlation between the model and field measurements. In most cases, the correlation was excellent.

Figures B-9 through B-14 show the effect of alkalinity supplement addition (in this case, NaOH) on final pH, percent ammonia remaining in solution and reaction time as a function of Cl_2:NH_3- and C_T. C_T is the total inorganic carbon (sum of CO_2, HCO_3^- and $CO_3^=$) in the system, expressed in moles per liter. The alkalinity supplement addition ("NaOH added") in each case refers to the NaOH added to solution beyond that required for neutralization of the acidity from hydrolysis and dissociation of the chlorine dosage (Equation 16, Table 3-3).

SECTION 6

PROCESS CONTROL

A breakpoint chlorination control system should be reliable and should facilitate the efficient use of chemicals and manpower. Chlorine overdosages can be quite expensive, with additional costs for chlorine and alkalinity supplement as well as dechlorinating agent. Chlorine and alkalinity costs alone can reach $800 per year for an overdosage of 1 mg/l in a 1 mgd application. Chlorine underdosages can result in significant reductions in ammonia removal efficiency and high combined chlorine residuals in the process effluent.

The nature of the breakpoint chlorination process is such that manual control is difficult, requiring the undivided attention of an operator. One aspect of this study was the evaluation of various process control systems and associated instrumentation.

PROCESS AND COMPONENT DESCRIPTIONS

The breakpoint chlorination process flow diagram is presented on Figure 6-1 and shows only those signals involved in control. The pilot plant control panel is shown on Figure 6-2. Principal signals generated and displayed are listed in Table 6-1.

The final control elements include the chlorinators and sodium hydroxide feeder, and the measured variables include ammonia, free chlorine residual, and pH analyzers and flowmeters.

Ammonia Analyzer

This device was a continuous on-line analyzer which utilized metered reagents in the colorimetric determination of ammonia. The calibrated accuracy was ±0.2 mg/l. Occasional drift was observed to be as high as 2 mg/l over a 12-hr period. "Noise" amplitudes as high as 3 mg/l, principally due to sample turbidity or occasional air bubbles, were observed. Disturbance durations ranged from seconds to several minutes. A sample filter was not used. Total dead time for the analyzer was about 17 min, consisting primarily of analysis time. (Dead time, in

process control, is the period of time after a force is applied during which no response is observed; it is the lag time between action and response.)

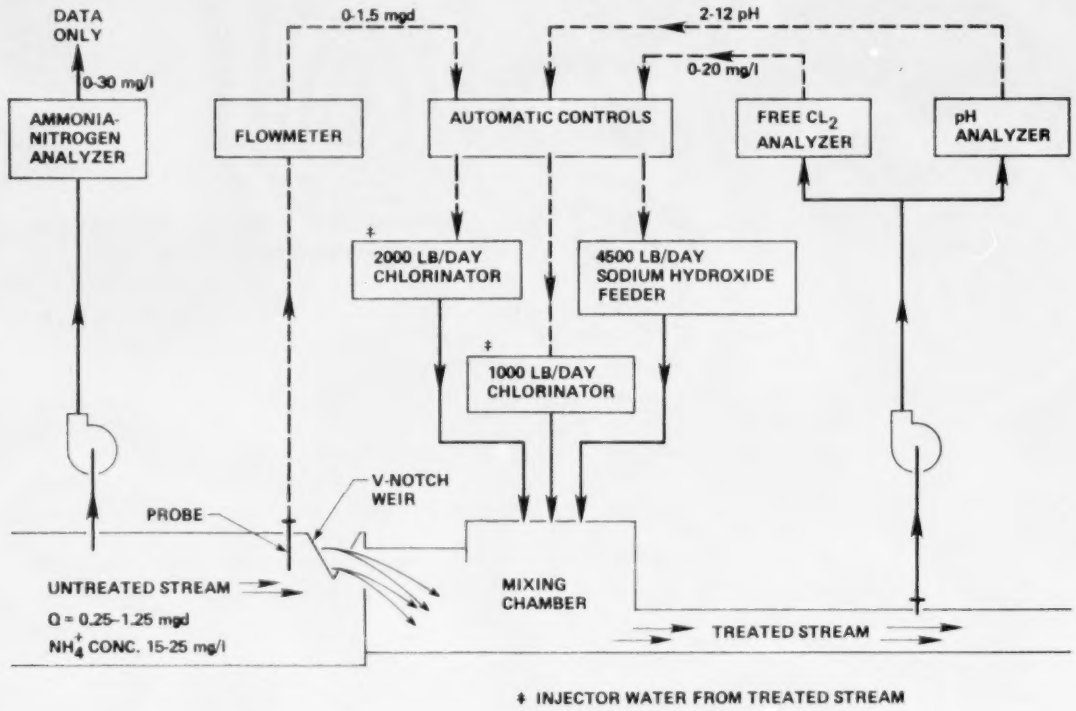


Figure 6-1 Simplified Process Diagram

Flowmeter

The flowmeter consisted of a level-measuring capacitance probe and appropriate circuits to convert level measurement to a linear flow signal. Calibrated accuracy was ±1 percent which was maintained for periods from one to several days. Zero and span drifts up to 0.2 mgd were observed. These were usually corrected by cleaning the probe of grease accumulations. The response of the flowmeter was essentially instantaneous. Hydraulic noise oscillations with amplitudes from 7 to 10 percent at periods from about 5 to 10 sec were transmitted. This noise was eliminated by appropriate electrical damping circuits.

Chlorinators

Chlorine was added to the process by vacuum injection into a liquid stream prior to the mixing chamber. Chlorine gas flow

was controlled by a linear variable orifice positioner in response to signals from the automatic controls. A constant but adjustable differential pressure was maintained across the linear variable orifice. All observations were based on flow as displayed on the gas flow rotameter. Repeatability was about ±1 percent. Maximum deviation from linearity over the range from 15 to 90 percent output was about 1-1/2 percent. Response dead band was about 1 percent. Full-scale output change required less than 1 minute.

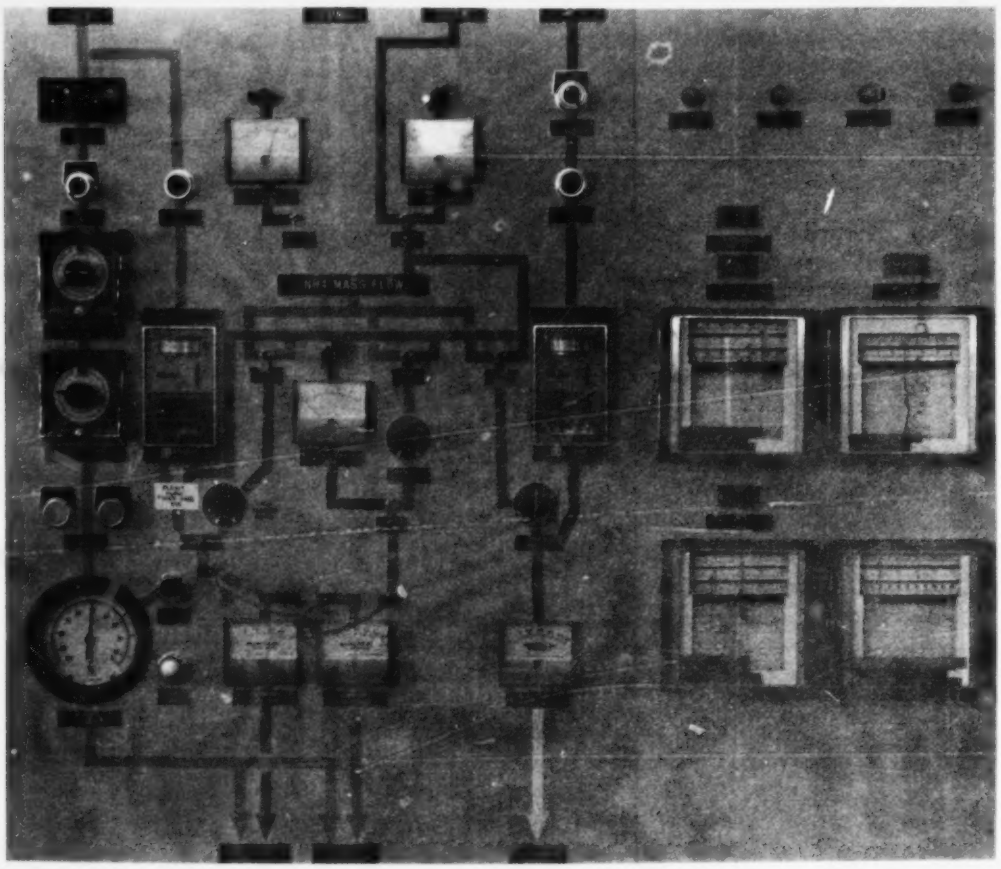


Figure 6-2 Control Panel

Electric linear flow transmitters were provided which operated with a maximum deviation from linearity of about 4 percent when used from 25 to 100 percent full-scale.

The chlorinators were also provided with dosage (ratio control) and vacuum controls. These controls were immobilized after calibration because of the non-linearity they induced in the response of the variable orifice control.

Free Chlorine Analyzer

This analyzer was a continuous amperometric titration unit, providing an electric signal proportional to free chlorine residual. The analyzer maintained an accuracy better than ±1 mg/l over a period of several months and was free of spurious noise. The dead time for this analysis consisted of a plant flow variant of 12 to 60 sec with an additional 2 minute fixed time for transit from the sampling point through the analyzer.

Table 6-1. Summary of Process Control Signals

Signal	Units	Notes
Free chlorine residual concentration	mg/l	(M)
Total chlorine residual concentration	mg/l	(M)
Sodium hydroxide feed rate	lbs/day	(M)(I)(T)
Plant flow (influent)	mgd	(M)(T)
pH	2 to 12	(M)
Gas flow, chlorinator No. 1	lbs/day	(M)
Gas flow, chlorinator No. 2	lbs/day	(M)
NH_4^+-N concentration	mg/l	(M)
NH_4^+-N flow rate	lbs/day	(C)(T)
Total chlorine gas flow rate	lbs/day	(C)(T)
Total CL_2 gas flow rate/NH_4^+-N flow rate	(none)	(C)

All of the above signals were recorded
(T) Integrated - totalized
(C) Computed
(M) Measured by transducer
(I) Inferred from speed measure

The useful range of the analyzer is limited at the low end to values about 3 to 4 mg/l because of interference from combined residuals below breakpoint. This in turn limits the minimum reliable process control set point to values of about 7 to 9 mg/l of free chlorine. These erroneous readings appeared to be consistent and repeatable and were equal to the sum of the free chlorine plus about 1/10 of the combined chlorine.

It is important that system design provide sufficient dead time at maximum plant flow rate to allow the reaction to go to completion before entering the analyzer; however, it is also important that this dead time be minimized because control

difficulties increase with dead time. Therefore, the chlorine residual analyzer was located at a distance downstream of the mixing chamber such that the travel time between the chamber and analyzer equaled the maximum reaction time.

pH Analyzer

The pH analyzer consisted of a glass measuring electrode, a reference electrode, and a thermistor temperature sensor mounted on a flow-through electrode holder. A signal preamplifier was externally mounted on the electrode holder to provide a continuous high-level temperature-compensated pH signal.

The analyzer was accurate to 0.1 pH units over a period of several months and was free of spurious noise. The accuracy of the pH signals was unaffected by the chlorine dosage either above or below breakpoint concentrations.

The dead time on the analysis consisted of a plant flow variant of 12 to 60 sec with an additional 20 sec fixed time for transit from the sampling point through the analyzer electrode holder. System design considerations for pH analyzer dead time are the same as those for the Free Chlorine Analyzer.

Sodium Hydroxide Feeder

The sodium hydroxide feed system consisted of a metering pump which fed a 50 percent solution from a liquid storage tank. The metering pump was a positive displacement unit with manual pump stroke control, and powered by a variable-speed d-c motor. Feed control was achieved by automatic motor speed variation in response to signals from the automatic control system. The local motor speed controller was a closed-loop system that compared motor speed as measured by a tachometer with the incoming automatic speed order.

Initial calibrated accuracy from 5 to 100 percent of output was ±1 percent. Some instability was observed for outputs below 5 to 6 percent. An output zero drift of about ±10 percent was observed after about 6 weeks of operation at which time the equipment was recalibrated and no further drift was observed.

System response was on the order of 2 sec for 5 to 100 percent without overshoot.

CONTROL REQUIREMENTS

The principal parameters for breakpoint chlorination control are free chlorine residual for chlorine dosage control and pH alkalinity supplement dosage control. The degree of resolution and repeatability of chemical feed rates is one of

the major factors which determines how efficiently the breakpoint process can be controlled.

At Rancho Cordova, the chlorine feed requirement varied from 160 lb/day to 2,300 lb/day. Control of free chlorine residual to ±3 mg/l required a control tolerance of about ±3 percent at minimum chlorine feed rates, and ±1 percent at maximum feed rates. The resolution of the chlorinators was about 1 percent, or about 10 lb/day on the small unit and 20 lb/day on the large one. At a minimum flow of 0.25 mgd, a feed-rate error of 10 lb/day would lead to free chlorine variations of about 4 mg/l. At maximum flows of 1.25 mgd, a feed-rate error of 10 lb/day gives an error of about 1 mg/l.

Previous discussion of the chemistry indicates that about 1.5 pounds of sodium hydroxide is required per pound of chlorine. This ratio is approximate and valid only if the untreated stream pH is near the desired reaction end point (i.e., all breakpoint acidity neutralized). The slope of the alkalinity curve at the control point determines the difficulty in obtaining proper control. A family of alkalinity curves is shown on Figure 6-3. pH control would be more difficult for wastewater with low alkalinity. The abscissas of these curves in relation to the pH control point could be interpreted as error of concentration or error of sodium hydroxide feed rate. At Rancho Cordova the minimum feed rate was about 250 lb/day, with maximum feed rates reaching about 3,450 lb/day.

If the pH/feed-rate curve is very nonlinear, a special nonlinear element should be inserted into the measurement loop to hold constant gain at all feed rates.

CONTROL SYSTEMS

Four systems were evaluated for their effect on breakpoint chlorination control: simple feedback control, simple feedback plus flow paced control, flow modified feedback plus flow paced control, NH_4^+ -N mass flow paced control.

Simple Feedback Control

Figures 6-4 and 6-5 show a simple feedback control system. This control system functions solely in response to deviations of free chlorine residual from the selected set point. Figure 6-5 shows a typical response (output) curve to an error signal. If the controller generates an output in response to a process error signal that will overcorrect to the extent that the new error is equal to or greater than the original eror and the new error is of opposite sign, then the output will violently oscillate. In terms of feed rate, if the analysis showed a deficiency of 10 lb/day and this provided a positive change in output of 20 lb/day or greater, then the system would oscillate.

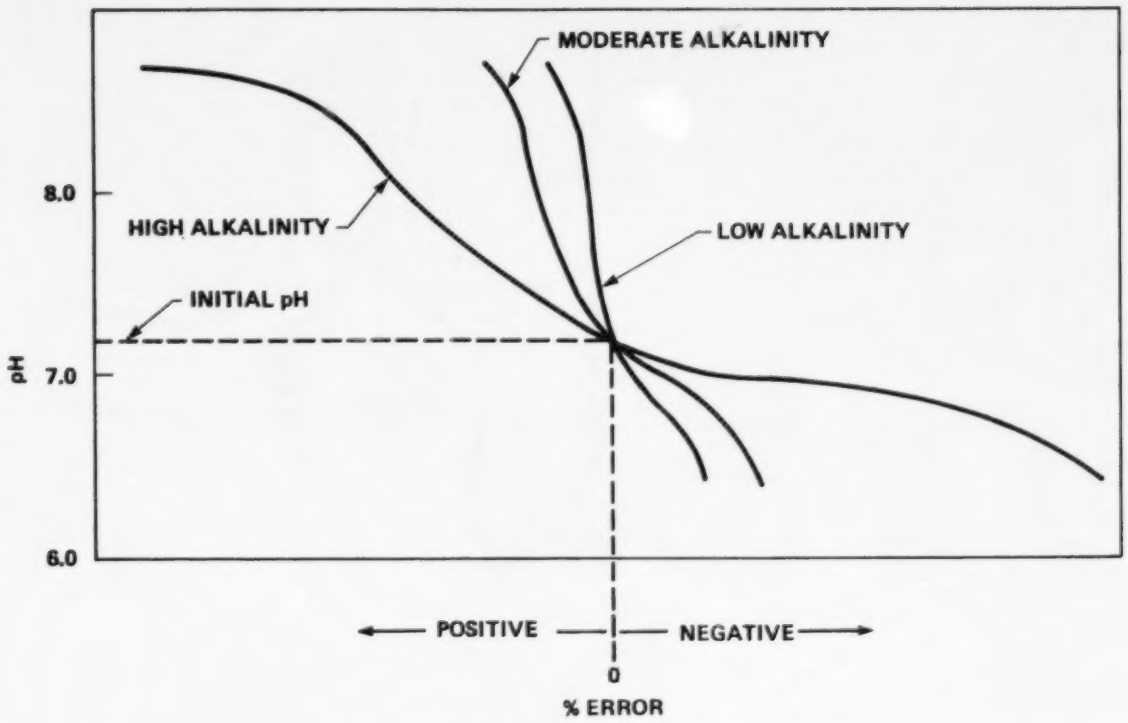
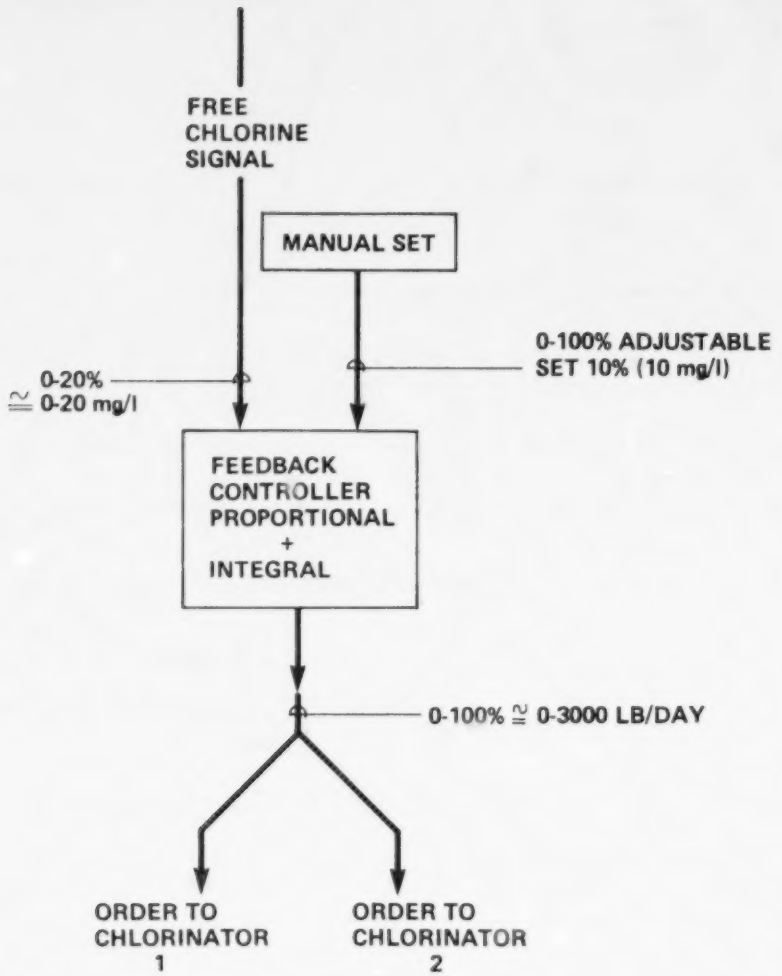


Figure 6-3 Typical pH Characteristics

Referring again to Figure 6-5, the output is continually changing as long as error is sensed by the controller. Since the output will continue to change until the results of the initial change are analyzed and returned to the controller, this effect must also be evaluated.

A conservative initial system design will provide for approximately half the feed rate correction to be made with the proportional band setting immediately ($-100\% \times \frac{\% \text{ ERROR}}{\% \text{ PB}}$, refer to Figure 6-4) with the remaining correction to be made over a period of time equal to twice the system dead time. Thus, an error signal indicating a deficiency of 10 lb/day feed rate would provide an increase in output of 5 lb/day immediately with the remaining 5 lb/day to be incremented over a period of time equal to twice the dead time.

A plant flow rate of 0.25 mgd with a free chlorine residual error of 1.0 mg/l requires a correction of 2.08 lb/day in chlorine feed rate. The same error at a plant flow rate of 1.25 mgd



$$\%\ \text{CONTROLLER OUTPUT} = C\% - 100\% \times \left[\frac{\%\ \text{ERROR}}{\%\ \text{PB}} + \frac{1}{\%\text{PB} \times T} \int_0^t \%\ \text{ERROR} \cdot dt \right]$$

% ERROR	=	SET % - SIGNAL %
% PB	=	% PROPORTIONING BAND ADJUSTMENT (ADJUSTABLE 0-200%)
T	=	RESET TIME ADJUSTMENT, MINUTES (ADJUSTABLE 0-20 MIN)
t	=	REAL TIME, MINUTES
C%	=	ADJUSTED VALUE AT t = 0

Figure 6-4 Simple Feedback Control - Chlorine Feeders

requires a correction of 10.41 lb/day in chlorine feed rate. Using simple feedback control, the control system response, as limited by stability criteria, is set for the maximum response at minimum flow. With a desired correction of 2.08 lb/day/mg/l free chlorine error at minimum flow, the correction should be 1.04 lb/day/mg/l error (immediate) plus 0.17 lb/day/min/mg/l error.

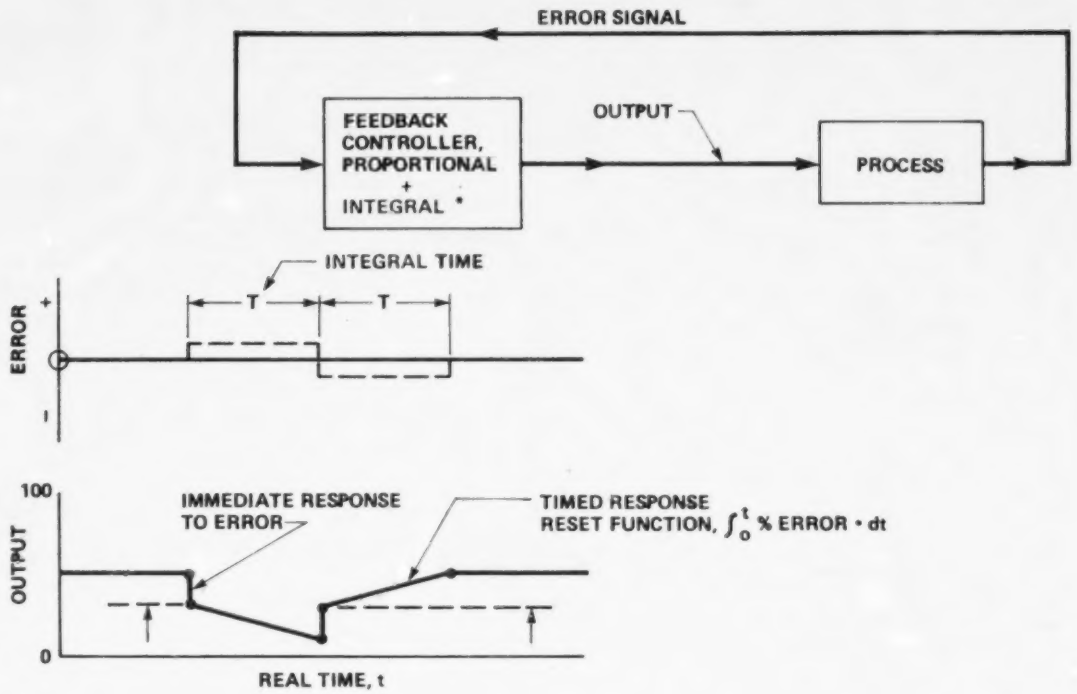


Figure 6-5 Control Response - Simplified Control Loop

At Rancho Cordova, plant flow varied from a minimum to maximum in a period of about five hours. These plant flow variations at median NH_4^+ -N concentrations required a chlorine feed rate variation from about 375 to 1,850 lb/day. The rate of change of chlorine feed rate was:

$$\frac{1,875 - 375}{5 \times 60} = 5 \text{ lb/day/min}$$

This value is conservative since, under some conditions, a 10 lb/day/min rate of change was required. Simple feedback control set for stability at minimum flow with an error of 3 mg/l

could only provide about 3 x 0.17 lb/day/min/mg/l error or about 0.51 lb/day/min. Therefore, simple feedback control could not keep up with required dosage variations and a compound control system was required.

Simple Feedback Plus Flow Paced Control

This compound system incorporated a flow paced control loop in addition to the free chlorine residual feedback loop. The control system is shown on Figures 6-6 and 6-7. This system

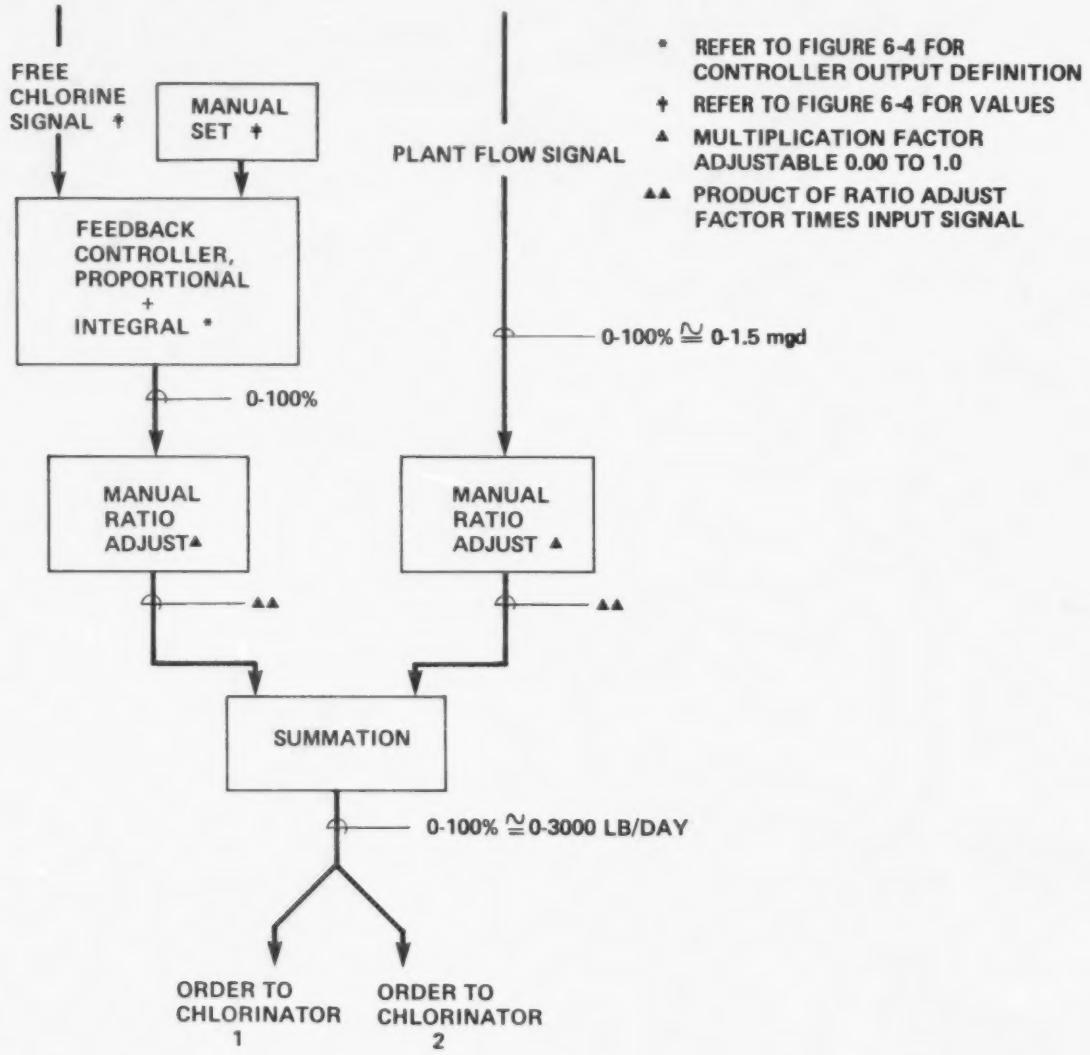

FREE CHLORINE SIGNAL †
MANUAL SET †
PLANT FLOW SIGNAL
* REFER TO FIGURE 6-4 FOR CONTROLLER OUTPUT DEFINITION
† REFER TO FIGURE 6-4 FOR VALUES
▲ MULTIPLICATION FACTOR ADJUSTABLE 0.00 TO 1.0
▲▲ PRODUCT OF RATIO ADJUST FACTOR TIMES INPUT SIGNAL
FEEDBACK CONTROLLER, PROPORTIONAL + INTEGRAL *
0-100% ≅ 0-1.5 mgd
0-100%
MANUAL RATIO ADJUST▲
MANUAL RATIO ADJUST ▲
▲▲
▲▲
SUMMATION
0-100% ≅ 0-3000 LB/DAY
ORDER TO CHLORINATOR 1
ORDER TO CHLORINATOR 2

Figure 6-6 Simple Feedback Plus Flow Paced Control - Chlorine Feeders

was satisfactory for sodium hydroxide feed maintaining the treated stream within ±0.3 pH units of the set point.

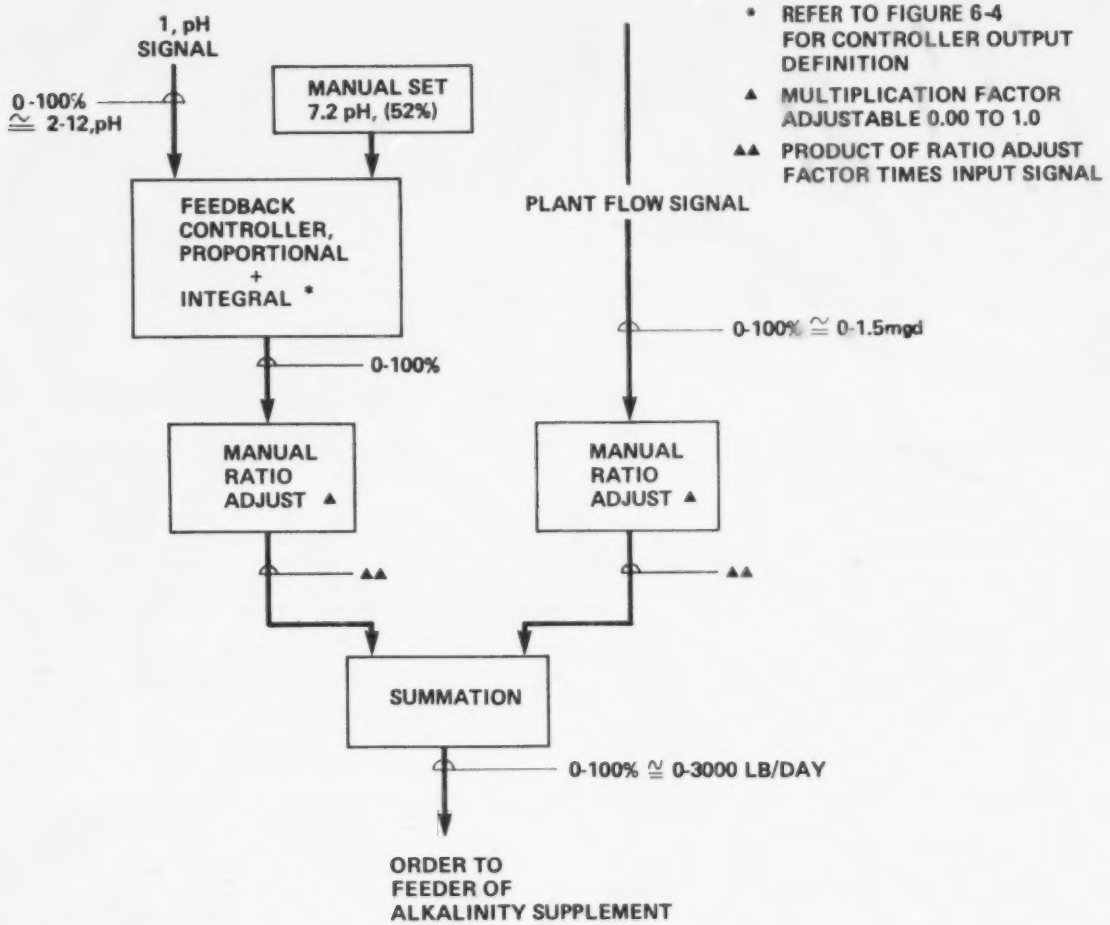

1, pH SIGNAL
0-100% ≅ 2-12,pH
MANUAL SET 7.2 pH, (52%)
FEEDBACK CONTROLLER, PROPORTIONAL + INTEGRAL *
0-100%
MANUAL RATIO ADJUST ▲
▲▲
PLANT FLOW SIGNAL
0-100% ≅ 0-1.5mgd
MANUAL RATIO ADJUST ▲
▲▲
SUMMATION
0-100% ≅ 0-3000 LB/DAY
ORDER TO FEEDER OF ALKALINITY SUPPLEMENT
* REFER TO FIGURE 6-4 FOR CONTROLLER OUTPUT DEFINITION
▲ MULTIPLICATION FACTOR ADJUSTABLE 0.00 TO 1.0
▲▲ PRODUCT OF RATIO ADJUST FACTOR TIMES INPUT SIGNAL

Figure 6-7 Simple Feedback Plus Flow Paced Control - Alkalinity Supplement

Figure 6-8 shows the effect of a Manual Ratio Adjust block in the plant flow signal line prior to the summation block. Optimum adjustment for direct plant flow paced signal should provide somewhat less dosage than is required for breakpoint at minimum NH_4^+ -N ion concentrations and Cl_2/NH_4^+ -N ratios. For a flow change of 1.0 mgd in 150 min, the chlorine feed rate would change at about 6 lb/day/min. At median chlorine dosages, a rate of change of chlorine feed of about 10 lb/day/min would be required. The feedback controller would, then, be required to supply the difference, or 4 lb/day/min in this example. The control error would be 4.0/0.17 or about 24 mg/l.

In these tests, free chlorine excursions, using this chlorination control system at plant flows above 0.5 mgd, were large and erratic and operation was generally unsatisfactory.

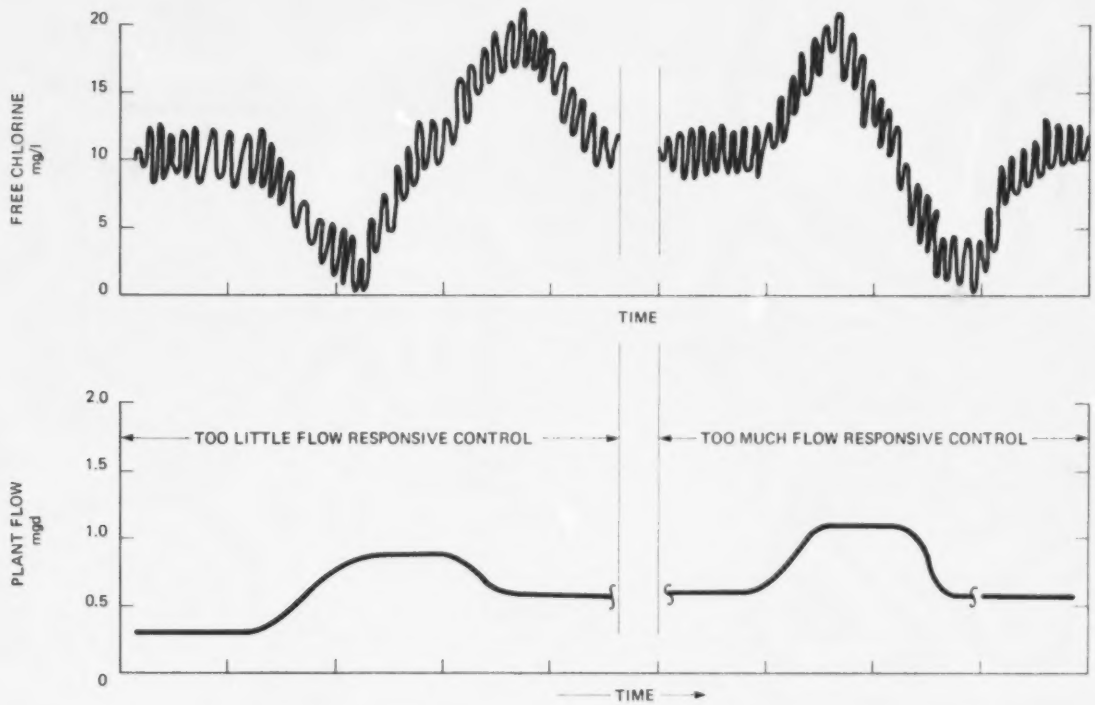


Figure 6-8 Effects of Flow Responsive Control on Free Chlorine Residual

Flow Modified Feedback Control Plus Flow Paced Control

This method of control is illustrated on Figure 6-9. The feedback controller and multiplier unit operate to provide control which is flow responsive and multiplies flow times chlorine dosage (chlorine dosage is the output of feedback control) to give a signal which is in units of lb/day of chlorine feed. Under steady state conditions, the controller provided 0.17 to 0.85 lb/day/min/mg/l error of free chlorine as a function of plant flow rates of 0.25 to 1.25 mgd. If the system is operating at the control point, flow changes do not cause upsets because the controller corrects only chlorine dosage errors.

The plant flow signal passing to the summation junction through the manual ratio adjust provides for an increment of direct plant flow paced control which was added to provide a

required increment of chlorinator capacity that was not obtainable through the flow modified feedback control portion. The flow modified feedback control was limited by scaling of the free chlorine signal and the proportional band adjustment of the controller.

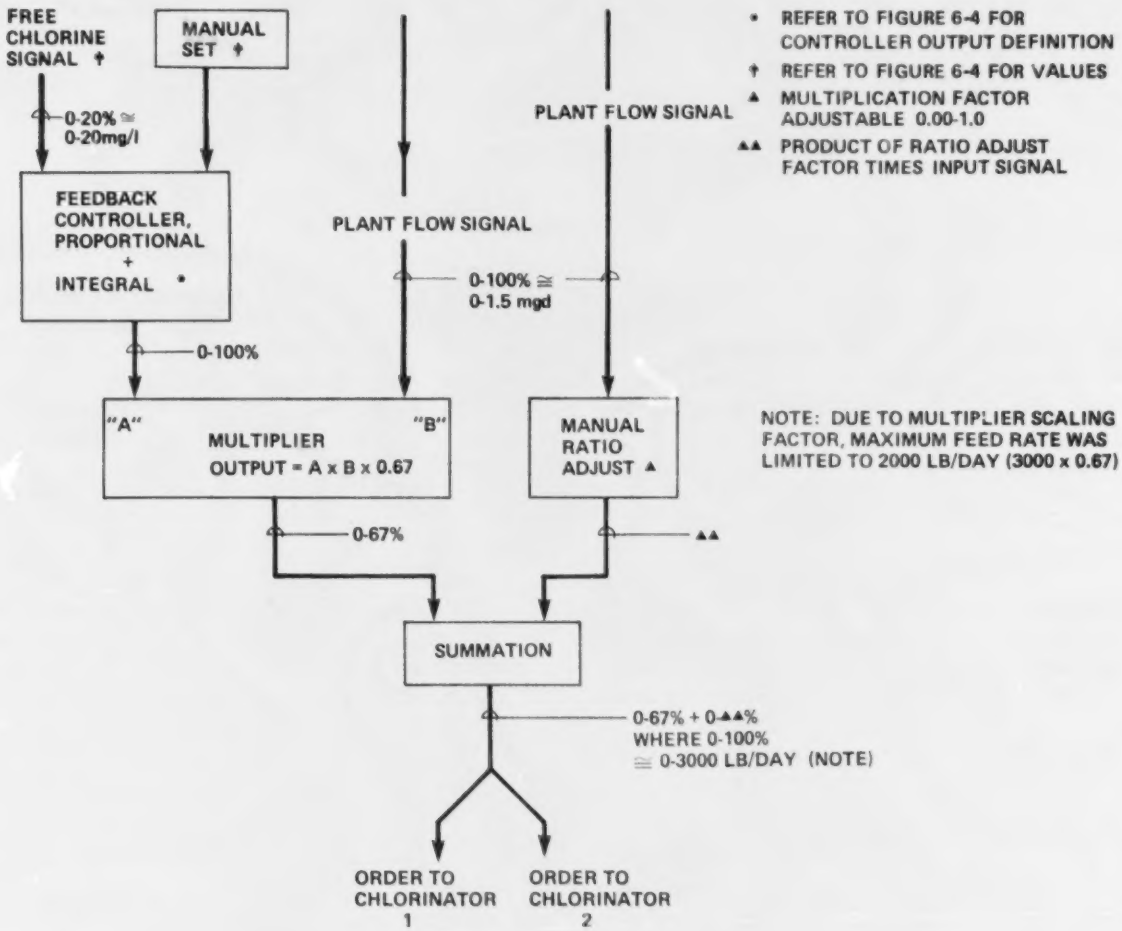

FREE CHLORINE SIGNAL †
MANUAL SET †
0-20% ≅ 0-20mg/l
FEEDBACK CONTROLLER, PROPORTIONAL + INTEGRAL *
0-100%
PLANT FLOW SIGNAL
0-100% ≅ 0-1.5 mgd
PLANT FLOW SIGNAL
"A"
"B"
MULTIPLIER
OUTPUT = A x B x 0.67
MANUAL RATIO ADJUST ▲
0-67%
▲▲
SUMMATION
0-67% + 0-▲▲%
WHERE 0-100% ≅ 0-3000 LB/DAY (NOTE)
ORDER TO CHLORINATOR 1
ORDER TO CHLORINATOR 2
* REFER TO FIGURE 6-4 FOR CONTROLLER OUTPUT DEFINITION
† REFER TO FIGURE 6-4 FOR VALUES
▲ MULTIPLICATION FACTOR ADJUSTABLE 0.00-1.0
▲▲ PRODUCT OF RATIO ADJUST FACTOR TIMES INPUT SIGNAL
NOTE: DUE TO MULTIPLIER SCALING FACTOR, MAXIMUM FEED RATE WAS LIMITED TO 2000 LB/DAY (3000 x 0.67)

Figure 6-9 Flow Modified Feedback Plus Flow Paced Control - Chlorine Feeders

Within the limits of signal output capacity, chlorinator control on flow modified feedback control only (with no contribution of direct plant flow signal) provided satisfactory control with free chlorine excursions of 5 to 6 mg/l from control point. These excursions were random and not particularly related to plant flow variations. Addition of direct plant flow control signal up to about one-half of the total control signal appeared to have little effect on the 5 to 6 mg/l excursions from the control set point.

Experience at Rancho Cordova showed that required chlorine dosages varied from about 120 mg/l to 250 mg/l as a function of NH_4^+ concentration and the NH_4^+ -N/Cl_2 ratio. For chlorine dosage variation of this magnitude over a 10-hour period, the rate of change of chlorine dosage was (250-120)/(10 x 60) = 0.217 mg/l/min. The flow modified feedback controller can increment 0.68 lb/day chlorine feed/min/mgd plant flow/mg/l of free chlorine error, or can correct for .0817 mg/l per minimum concentration change for a free chlorine residual error input signal of 1.0 mg/l. Control offset from set point would then be:

$$\frac{0.217 \text{ mg/l/min}}{0.0817/\text{min}} = 2.5 \text{ mg/l error}$$

Ammonia Nitrogen Mass Flow Paced Control

In this control mode, NH_4^+ -N concentration was measured and continuously multiplied by plant flow to provide an NH_4^+ -N mass flow rate (lb/day). This flow rate was used as a direct feed forward signal in lieu of plant flow in several control schemes for chlorine and sodium hydroxide feed. NH_4^+ -N concentration, as a raw signal, was not suitable for control due to the presence of noise. This signal was conditioned by resistance-capacitance filtering which added a 5-min time constant to the 17-min analysis dead time.

After conditioning, the signal was used for control. No improvement in control was noted. Control overshoots were occasionally noted that appeared to be coincidental with changes in the rate of change of NH_4^+ -N concentration. These overshoots were the probable result of the analysis dead time and signal conditioning time which introduced out-of-phase signals into the control system.

RECOMMENDED CONTROL SYSTEM

Based on the preceeding discussion of process control systems, a control scheme was selected for both alkalinity supplement feed and chlorine feed.

Alkalinity Supplement Feed Control

Sodium hydroxide feed control at Rancho Cordova was satisfactory with the control system shown on Figure 6-7. However, a flow modified feedback control with plant flow paced control as shown on Figure 6-10 is recommended. This control configuration will provide better pH control in breakpoint applications with low influent alkalinity. The direct plant flow paced portion of the total control signal should be less than the ratio of breakpoint chlorine dosages for minimum to maximum process requirements.

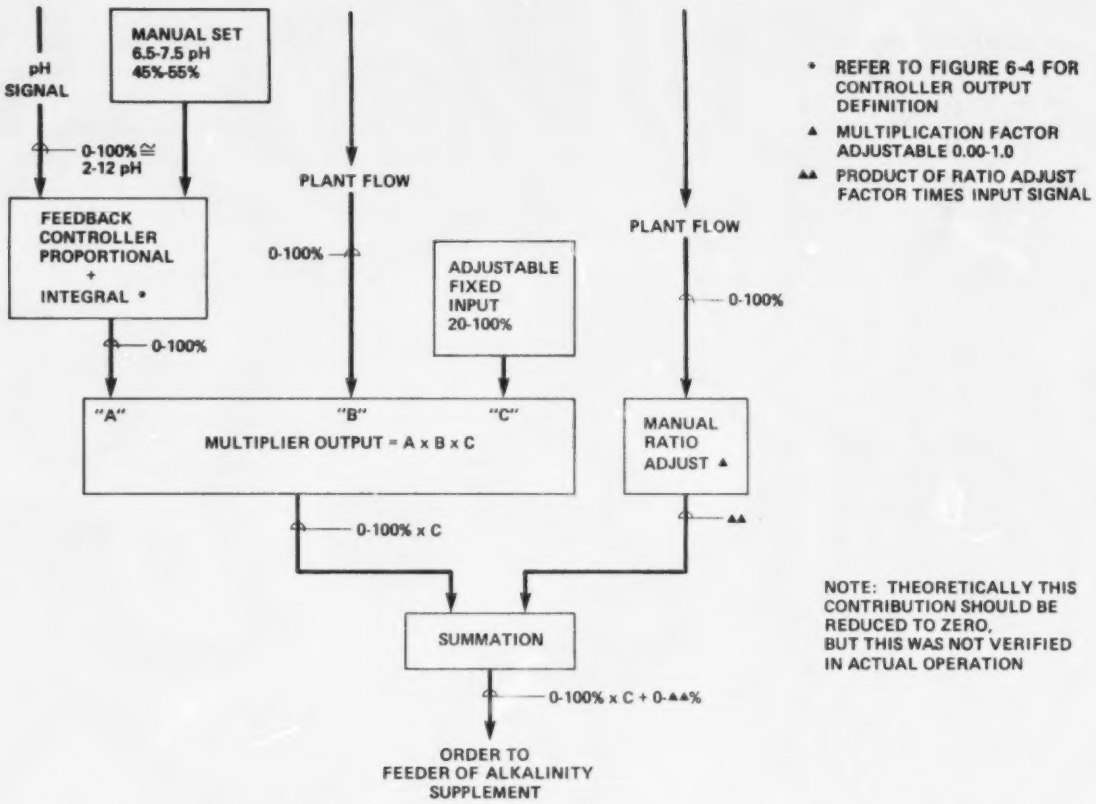

pH SIGNAL
MANUAL SET 6.5-7.5 pH 45%-55%
0-100% ≅ 2-12 pH
FEEDBACK CONTROLLER PROPORTIONAL + INTEGRAL •
0-100%
PLANT FLOW
0-100%
ADJUSTABLE FIXED INPUT 20-100%
PLANT FLOW
0-100%
"A"
"B"
"C"
MULTIPLIER OUTPUT = A x B x C
MANUAL RATIO ADJUST ▲
0-100% x C
▲▲
SUMMATION
0-100% x C + 0-▲▲%
ORDER TO FEEDER OF ALKALINITY SUPPLEMENT
• REFER TO FIGURE 6-4 FOR CONTROLLER OUTPUT DEFINITION
▲ MULTIPLICATION FACTOR ADJUSTABLE 0.00-1.0
▲▲ PRODUCT OF RATIO ADJUST FACTOR TIMES INPUT SIGNAL
NOTE: THEORETICALLY THIS CONTRIBUTION SHOULD BE REDUCED TO ZERO, BUT THIS WAS NOT VERIFIED IN ACTUAL OPERATION

Figure 6-10 Recommended Control - Alkalinity Supplement

Chlorine Feed Control

The recommended system for control of chlorine feed equipment is shown on Figure 6-11. Two chlorinators are used, one large and one small. For this configuration, the large chlorinator is controlled solely by plant flow rate and the small chlorinator is controlled by a flow modified feedback controller.

The recommended control scheme of Figure 6-11 showed average excursions from the free residual control point of about ±3 mg/l free chlorine. The excursions were somewhat larger at low plant flows and low NH_4^+ -N concentrations than they were at higher flows and concentrations.

The chlorinator feed rate resolution is suggested as an important element in the superior performance of the recommended

chlorine control mode. The difference may occur because the large chlorinator in the recommended scheme is not called upon to make both positive and negative adjustments in any short period of time since it is totally flow responsive. The flow signal, as previously noted, was conditioned to remove noise. This would tend to minimize any errors due to lack of resolution of the large chlorinator feed rate, because over any period of time changes in feed rate would tend to be unidirectional and infrequent.

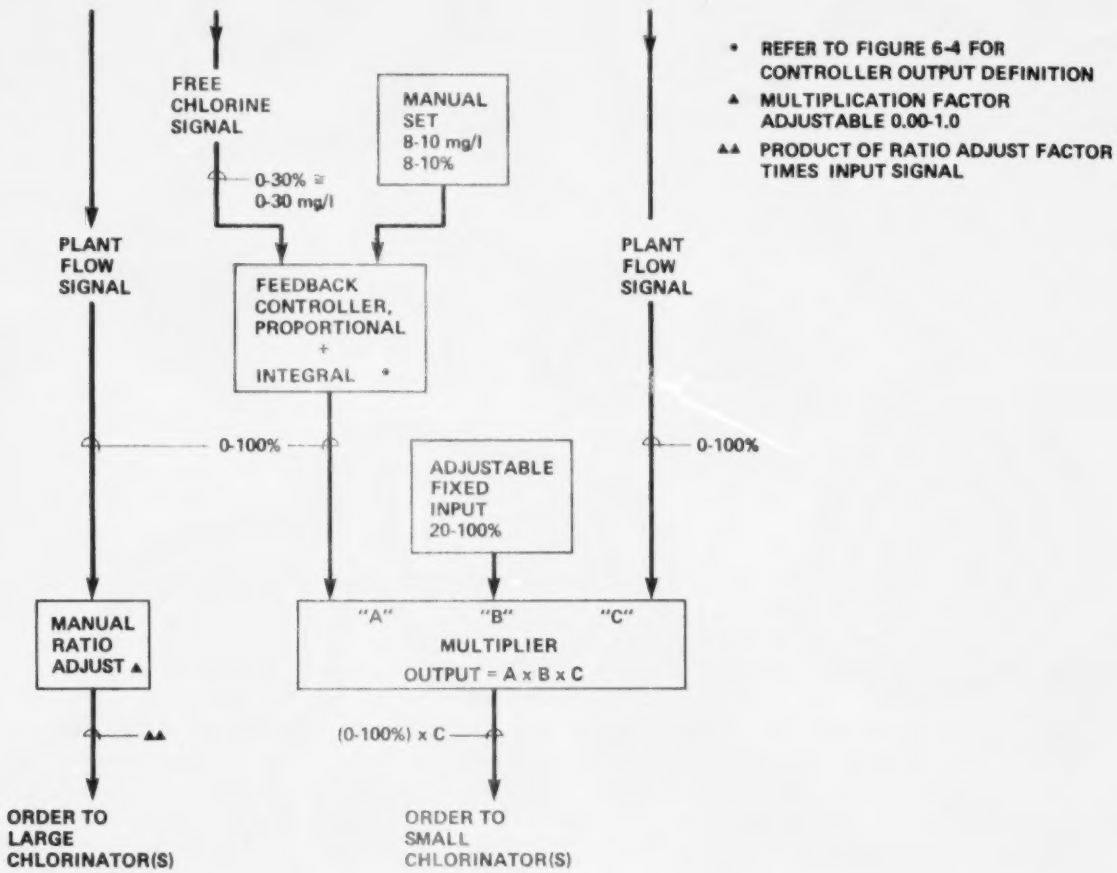

• REFER TO FIGURE 6-4 FOR CONTROLLER OUTPUT DEFINITION
▲ MULTIPLICATION FACTOR ADJUSTABLE 0.00-1.0
▲▲ PRODUCT OF RATIO ADJUST FACTOR TIMES INPUT SIGNAL
FREE CHLORINE SIGNAL
MANUAL SET 8-10 mg/l 8-10%
0-30% ≅ 0-30 mg/l
PLANT FLOW SIGNAL
FEEDBACK CONTROLLER, PROPORTIONAL + INTEGRAL •
PLANT FLOW SIGNAL
0-100%
ADJUSTABLE FIXED INPUT 20-100%
0-100%
MANUAL RATIO ADJUST ▲
"A" "B" "C"
MULTIPLIER
OUTPUT = A x B x C
▲▲
(0-100%) x C
ORDER TO LARGE CHLORINATOR(S)
ORDER TO SMALL CHLORINATOR(S)

Figure 6-11 Recommended Control - Chlorine Feeders

To obtain optimum response from the chlorinators, the control vacuum should be reduced until full linear travel of the variable orifice produces only the minimum quantity required to meet the current maximum process requirements. The small chlorinators should be carefully sized to provide 125 to 150 percent of the amount of chlorine feed needed between anticipated

maximum and minimum breakpoint chlorine dosages. The large chlorinators should be sized to provide breakpoint concentrations of chlorine for maximum plant flows and minimum NH_4^+ -N concentrations and Cl_2:NH_4^+ -N ratios.

INSTRUMENTATION REQUIREMENTS

Control Components

Since process control is critical, requiring a chlorine feed rate resolution of 1 percent or better, control components which have dead bands should be avoided.

Drift In Zero and Linearity

Since breakpoint process control depends partly on feed forward flow signals, zero or linearity errors have to be compensated for through the feedback controller. Zero drift in control components causes system gain changes which can result in severe control problems at low plant flow rates. Components should be selected which are as linear and drift-free as possible and should be readily adjustable to eliminate zero and linearity errors.

Feedback Controller Scaling

Control loop and component characteristics should be carefully analyzed to allow the initial calculated proportional band for the controller to be about 40 percent at the point where oscillations will first commence. If this requirement cannot be met by appropriate scaling of free chlorine residual or pH signal alone, then an additional attenuator (or amplifier) must be added directly in the feedback controller output to the multiplier and the multiplier (or divider) appropriately rescaled. Full signal range must be retained in the multiplier output.

Signal Redundancy

If the process is required to run on a continuous basis, redundant automatic plant flow, free chlorine residual and pH input signals will be required to maintain operation while these transmitters are routinely cleaned, serviced and adjusted.

Calibration Signals

To initially align the control system and to periodically check its proper operation after startup, calibration input signals will be simultaneously required for free chlorine residual, plant flow and pH. It is recommended that these calibration signals be permanently built into the control system

with appropriate readouts, stepless 0 to 100 percent adjustments and "operate-calibrate" selector switches. Plant flow calibration inputs should have separate "operate-calibrate" switches for each input into each chlorinator control and alkalinity supplement feed control system.

SUMMARY

The control system can provide satisfactory control only if it is properly tailored to the application. Oversizing of feed capacity will proportionately reduce the control tolerances. Prior to finalizing system design, data should be collected on plant flow covering maximum and minimum values and maximum rates of change. Data should also be available on NH_4^+ -N concentration maximums, minimums and maximum rates of change. Alkalinity data should also be collected to determine the system's response to addition of alkalinity supplement.

REFERENCES

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APPENDICES

APPENDIX A

RANCHO CORDOVA BREAKPOINT CHLORINATION DEMONSTRATION PROGRAM

DATA SUMMARY

Time	Cl_2 feed, lb/day	Flow, mgd	Cl_2 dose, mg/l	Initial NH_4^+-N, mg/l	$(Cl_2/NH_4^+$-N)	Free residual remaining, mg/l	Final NH_4^+-N, mg/l	Initial NO_2^--N, mg/l	Initial NO_3^--N, mg/l	Final NO_3^--N, mg/l	NO_3^- prod. in B'point, mg/l	Chlorine consumed by reaction *				Unidentified loss, mg/l
												$NH_4^+ \rightarrow N_2$ mg/l	$NH_4^+ \rightarrow NC_3$ mg/l	$NO_2^- \rightarrow NO_3^-$ mg/l	$NH_4^+ \rightarrow NCl_3$ mg/l	
I. pH set point 6.5 Breakpoint effluent used as injector water, March 10, 1976																
1450	2030	1.204	202	20.25	10.0	9.5	1.4*	0.27	0.20	1.2	0.73	143	15	1	21	12
1510	2100	1.204	209	20.25	10.3	9.5	1.8*	0.21	0.17	1.4	1.02	140	21	1	27	19
1530	2075	1.171	212	19.31	11.0	15	2.3*	0.15	0.15	1.2	0.90	129	18	1	35	14
1545	1900	1.108	206	18.27	11.3	17	1.4*	0.07	0.08	1.3	1.15	126	23	0	21	17
			$\bar{X}$ =207	$\bar{X}$ =19.5	$\bar{X}$ =10.6	$\bar{X}$ =13					$\bar{X}$ =0.95	$\bar{X}$ =135	$\bar{X}$ =19	$\bar{X}$ =1	$\bar{X}$ =26	$\bar{X}$ =19
			SD= 4	SD= 0.9	SD= 0.6	SD= 4					SD=0.18	SD= 8	SD= 4	SD=1	SD= 7	SD= 3
II. pH set point 7.0 Secondary effluent used as injector water, February 20,1976																
0020	1625	0.944	206	22	9.4	16	0.56								9	
0105	1300	0.774	201	22	9.1	15	-								5	
0202	920	0.544	203	22.5	9.0	16.5	0.34								6	
0301	670	0.404	199	22	9.0	8	0.38								4	
0403	560	0.324	207	21.5	9.6	12	0.29								6	
0703	625	0.374	200	20.1	9.9	9	0.38								8	
0755	1300	0.684	186	19.5	9.5	10	0.53								4	
0907	1670	1.104	181	19.5	9.3	11.5	0.29								7	
1001	1700	1.174	182	19.5	9.3	9	0.47								4	
1104	1820	1.174	186	20.0	9.9	6	0.26								11	
1200	1830	1.044	213	23	9.1	9	0.75									
			$\bar{X}$ =196	$\bar{X}$ =21.1	$\bar{X}$ =9.5	$\bar{X}$ =11	$\bar{X}$ =0.43									
			SD= 11	SD= 1.3	SD=0.3	SD= 4	SD=0.15									
III. pH set point 7.0 Secondary effluent used as injector water, March 3-4, 1976																
1953	1390	1.124	202	19	10.6	12.5	0.68	0.38	0.38	1.5	1.04	139	21	2	10	17
2051	1910	1.078	214	19	11.3	14	0.75	0.28	0.35	1.3	1.05	139	21	1	11	28
2154	1930	1.174	167	19	8.8	13	0.82	0.11	0.33	1.3	1.16	138	24	1	12	(-3)
2252	1750	1.174	161	16	10.1	16	0.80	0.09	0.03	1.2	1.08	131	22	0	12	1
0002	1330	1.094	150	17	8.8	10	-	0.06	0.05	-	-	-	-	0	-	-
0815	1045	0.1066	190	17	11.2	11.5	0.52	0.04	0.05	1.1	0.98	125	20	0	8	25
0158	790	0.526	175	17	10.3	13	0.04	0.07	0.06	1.2	1.07	125	22	0	9	10
3251	550	0.354	160	16.5	11.3	16	0.50	0.07	0.01	1.4	1.29	122	26	0	8	14
0351	440	0.304	170	16	11.0	18.5	0.73	0.06	0.05	1.3	1.21	116	25	0	11	5
0451	376	0.284	138	16	9.9	20	0.76	0.09	0.04	1.2	1.09	116	22	0	12	(-12)
0552	376	0.284	156	16	9.9	12	0.50	0.10	0.04	1.2	1.06	118	22	1	8	(-3)
0651	499	0.394	166	15	11.1	10	0.43	0.10	0.04	1.3	1.06	111	22	1	7	15
0800	800	0.624	154	14	11.0	12	0.75	0.27	0.10	2.0	1.63	101	32	1	11	(-4)
			$\bar{X}$ =177	$\bar{X}$ =16.9	$\bar{X}$ =10.5	$\bar{X}$ =14	$\bar{X}$ =0.65				$\bar{X}$ =1.14	$\bar{X}$ =123	$\bar{X}$ =23	$\bar{X}$ =1	$\bar{X}$ =10	$\bar{X}$ =8
			SD= 19	SD= 1.6	SD= 0.8	SD= 3	SD=0.14				SD=0.17	SD= 12	SD=23	SD=1	SD= 2	SD=12

Table A-1. Rancho Cordova Breakpoint Chlorination-Data Summary

Time	Cl_2 feed, lb/day	Flow, mgd	Cl_2 dose, mg/l	Initial NH_4^+-N, mg/l	(Cl_2/NH_4^+-N)	Free residual remaining, mg/l	Final NH_4^+-N, mg/l	Initial NO_2^--N, mg/l	Initial NO_3^--N, mg/l	Final NO_3^--N, mg/l	NO_3^- prod. in B'point, mg/l	Chlorine consumed by reaction: $NH_4^+ \rightarrow N_2$ mg/l	$NH_4^+ \rightarrow NO_3^-$ mg/l	$NO_2^- \rightarrow NO_3^-$ mg/l	$NH_4^+ \rightarrow NCl_3$ mg/l	Unidentified loss, mg/l
V. pH set point 7.3 Breakpoint effluent used as injector water, March 10, 1976																
0405	300	0.314	115	9.5	12.1	20	0.39	0.23	0.27	1.1	0.60	69	12	1	6	7
0450	300	0.314	115	9.8	11.7	15	0.29	0.28	0.26	1.5	0.96	72	19	1	4	4
0552	290	0.304	114	9.5	12.0	10	0.33	0.34	0.26	1.6	1.00	70	20	2	5	7
0652	340	0.362	113	10.0	11.3	6	0.15	0.41	0.31	1.6	0.88	75	18	2	2	10
0750	1185	0.934	152	14.0	10.9	15	0.48	0.48	0.37	2.1	1.25	103	25	2	7	0
0859	1375	1.174	140	14.0	10.0	16	0.50	0.67	0.59	2.5	1.24	103	25	3	8	(-18)
1002	1340	1.104	146	13.9	10.5	12.5	0.20	0.85	0.79	2.6	0.96	104	19	4	3	3
1102	1610	1.174	164	15.5	10.6	11	0.37	0.84	1.05	2.4	0.51	115	10	4	6	18
1200	1950	1.304	175	18.2	9.6	19	-	0.83	1.30	-	-	-	-	3	-	-
			$\bar{X}$ =137	$\bar{X}$ =12.7	$\bar{X}$ =11.0	$\bar{X}$ =13	$\bar{X}$ =0.34				$\bar{X}$ =0.93	$\bar{X}$ = 89	$\bar{X}$ =14	$\bar{X}$ =3	$\bar{X}$ =5	$\bar{X}$ = 4
			SD= 24	SD= 3.1	SD= 0.9	SD= 4	SD=0.12				SD=0.27	SD= 19	SD= 5	SD=1	SD=2	SD= 8
V. pH set point 7.5 Secondary effluent used as injector water, March 2-3, 1976																
2100	2020	1.114	217	18	12.1	18	0.75	0.01	0.09	1.4	1.31	131	27	0	11	33
2153	1815	1.104	197	17.7	11.1	17	0.75	0.01	0.07	1.4	1.33	129	27	0	11	13
2255	1690	1.104	184	17	10.8	14	0.76	0.01	0.06	1.2	1.14	124	23	0	12	11
0001	1460	0.934	187	17	11.0	14	0.72	0.01	0.06	1.2	1.15	124	23	0	11	15
0051	1190	0.774	184	17	10.9	12.5	0.65	0.01	0.05	1.1	1.05	124	21	0	10	16
0157	800	0.524	183	17	10.8	12.5	0.55	0.01	0.05	0.92	0.87	125	18	0	8	19
0250	570	0.374	183	17	10.8	12.5	0.39	0.01	0.05	1.1	1.06	126	22	0	6	16
0351	505	0.324	187	17	11.0	15	0.49	0.01	0.06	1.2	1.14	126	23	0	7	16
0451	470	0.304	185	17	10.9	14	0.44	0.01	0.07	1.2	1.15	126	23	0	7	15
0552	430	0.284	182	17	10.7	20	0.50	0.01	0.06	1.3	1.24	126	25	0	8	3
0651	530	0.364	175	16	10.9	12.5	0.46	0.01	0.06	1.3	1.24	118	25	0	7	12
0800	1050	0.734	172	16	10.7	15	0.52	0.01	0.07	1.3	1.23	118	25	0	8	6
0905	1430	1.014	169	16	10.6	14.5	0.53	0.02	0.08	1.5	1.40	118	28	0	8	0
1000	1270	0.994	153	16	9.6	12.5	0.45	0.02	0.08	1.8	1.70	119	34	0	7	(-19)
			$\bar{X}$ =183	$\bar{X}$ =16.8	$\bar{X}$ =10.8	$\bar{X}$ =14	$\bar{X}$= 0.57				$\bar{X}$ =1.18	$\bar{X}$ =124	$\bar{X}$ =25	$\bar{X}$ =0	$\bar{X}$ =9	$\bar{X}$ =11
			SD= 14	SD= 0.6	SD= 0.5	SD= 2	SD=0.13				SD=0.14	SD= 4	SD= 4	SD=-	SD=2	SD=12
VI. pH set point 7.7 Breakpoint effluent used as injector water, March 11, 1976																
0310	300	0.374	96	9.8	9.8	7	0.70	0.07	0.05	1.1	0.98	69	20	0	11	(-11)
0342	250	0.324	93	8.9	10.4	7	0.70	0.07	0.06	1.2	1.07	62	22	0	11	(-9)
0443	230	0.304	91	8.4	10.8	12	0.17	0.06	0.06	1.2	1.08	63	22	0	3	(-9)
0555	200	0.304	79	7.9	10.0	12	0.64	0.03	0.06	1.2	1.11	55	23	0	10	(-21)
0648	250	0.374	80	9.2	8.7	9	0.16	0.01	0.06	1.1	1.04	69	21	0	2	(-21)
0800	940	0.824	137	11.8	11.6	16	0.57	0.01	0.06	1.1	1.04	85	21	0	9	6
0900	1230	1.104	134	12.2	11.0	13.5	0.62	0.01	0.06	1.1	1.04	88	21	0	9	2
1000	1290	1.164	133	11.8	11.3	12.5	0.43	0.10	0.13	1.6	1.37	86	28	1	7	(-2)
1100	1580	1.304	145	12.9	11.2	10	0.31	0.27	0.19	1.7	1.24	96	25	1	5	8
1200	1620	1.234	157	15.0	10.5	10	0.88	0.15	0.20	2.4	2.05	107	42	1	13	(-16)
1300	1570	1.019	185	16.3	11.3	11.5	0.86	0.03	0.21	1.6	1.36	117	28	0	13	15
1400	1800	1.044	207	17.7	11.7	13	0.14	0.03	0.20	1.1	0.87	134	18	0	2	40
			$\bar{X}$ =128	$\bar{X}$ =11.8	$\bar{X}$ =10.7	$\bar{X}$ =11	$\bar{X}$ =0.52				$\bar{X}$ =1.19	$\bar{X}$ = 86	$\bar{X}$ =24	$\bar{X}$ =0	$\bar{X}$ =8	$\bar{X}$ =(-1)
			SD= 42	SD= 3.2	SD= 0.9	SD= 3	SD=0.27				SD=0.31	SD= 24	SD= 6	SD=1	SD=4	SD=17

Table A-1. (Continued)

Time	Cl_2 feed, lb/day	Flow, mgd	Cl_2 dose, mg/l	Initial NH_4^+-N, mg/l	$(Cl_2/NH_4^+$-N)	Free residual remaining, mg/l	Final NH_4^+-N, mg/l	Initial NO_2^--N, mg/l	Initial NO_3^--N, mg/l	Final NO_3^--N, mg/l	NO_3^- prod. in B'point, mg/l	Chlorine consumed by reaction: $NH_4^+ \rightarrow N_2$, mg/l	$NH_4^+ \rightarrow NO_3^-$, mg/l	$NO_2^- \rightarrow NO_3$, mg/l	$NH_4^+ \rightarrow NCl_3$, mg/l	Unidentified loss, mg/l
VII. pH set point 8.0	Secondary effluent used as injector water, March 4-5, 1976															
1655	1435	0.824	209	21	9.9	7	0.52	0.01	0.05	1.0	0.94	156	19	0	8	19
1753	1600	0.924	208	20.8	10.0	11	0.54	0.01	0.05	1.0	0.94	154	19	0	8	16
1813	1550	0.924	201	21	9.6	12.5	0.83	0.01	0.05	1.2	1.15	153	23	0	13	(-1)
1855	1750	1.000	210	20.5	10.2	11.5	1.02	0.01	0.05	1.0	0.95	148	19	0	16	15
2055	2080	1.234	202	21	9.6	11.5	0.97	0.01	0.05	0.78	0.73	152	15	0	15	8
2155	2010	1.174	205	19.8	10.4	14	0.93	0.05	0.05	0.68	0.59	144	12	0	14	21
2255	1950	1.104	206	20	10.3	16	0.88	0.01	0.04	0.58	0.54	145	11	0	13	21
2354	1370	0.884	186	19.5	9.5	9	-	-	-	-	-	-	-	-	-	-
0052	1135	0.714	191	19	10.0	13	0.58	0.01	0.01	0.64	0.64	140	13	0	9	16
0148	855	0.524	196	19	10.3	12.5	0.56	0.01	0.04	0.70	0.66	140	13	0	9	21
0249	625	0.384	195	19	10.3	10	-	0.01	0.05	-	-	-	-	0	-	-
0348	515	0.324	191	18.7	10.2	7	0.43	0.01	0.04	0.75	0.73	139	14	0	7	24
0450	490	0.284	207	18.5	11.2	12	-	0.01	0.05	0.82	0.77	-	16	0	-	-
			$\bar{X}$ =201	$\bar{X}$ =19.8	$\bar{X}$ =10.1	$\bar{X}$ =11	$\bar{X}$ =0.73				$\bar{X}$ = 0.78	$\bar{X}$ =147	$\bar{X}$ =16	$\bar{X}$ =0	$\bar{X}$ =11	$\bar{X}$ =16
			SD= 8	SD= 1.0	SD= 0.4	SD= 3	SD=0.22				SD= 0.19	SD= 6	SD= 4	SD=-	SD= 3	SD= 7
VIII. pH set point 8.5	Breakpoint effluent used as injector water, March 10, 1976															
1708	1450	0.906	192	17.7	10.8	14	0.52	0.07	0.08	1.4	1.25	131	25	1	8	13
1730	1430	0.876	196	17.2	11.4	14	1.3*	0.13	0.09	1.2	0.93*	-	-	-	-	-
1750	1445	0.933	186	16.9	11.0	19.5	1.3*	0.04	0.08	0.94	0.82*	-	-	-	-	-
1815	1410	0.933	181	16.9	10.7	15	1.3*	0.03	0.07	0.78	0.69*	-	-	-	-	-
			$\bar{X}$ =189	$\bar{X}$ =17.2	$\bar{X}$ =17.2	$\bar{X}$ =16										
			SD= 7	SD= 0.4	SD= 0.4	SD= 3										

Table A-1. (Continued)

APPENDICES

APPENDIX B

RANCHO CORDOVA BREAKPOINT CHLORINATION DEMONSTRATION PROGRAM

BREAKPOINT MODEL PREDICTIONS

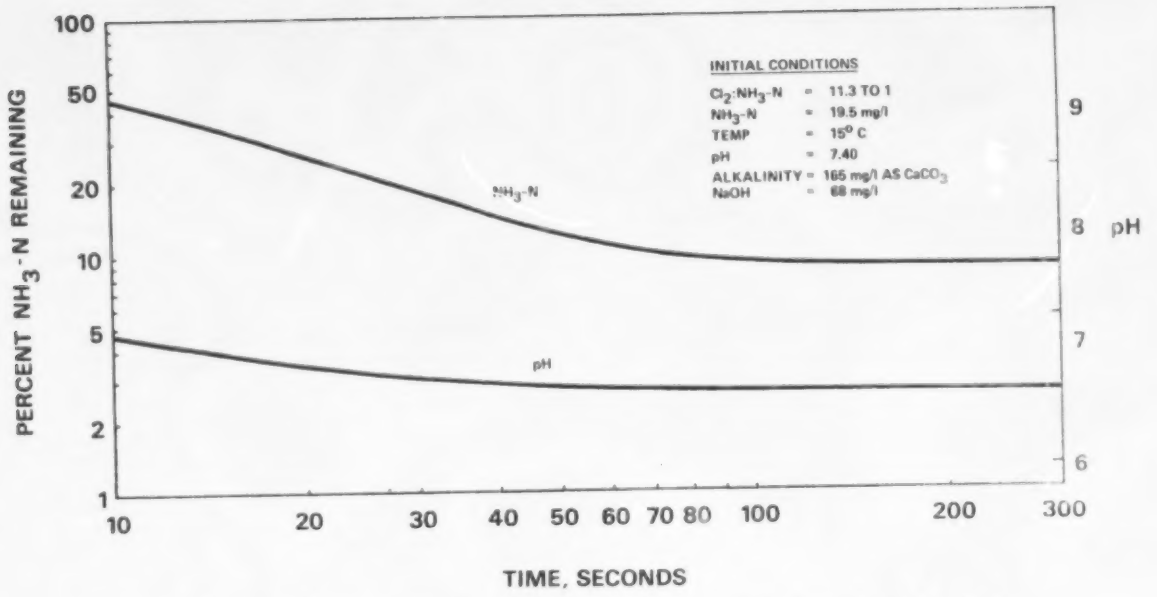

Figure B-1. Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor-Model Prediction-pH Set Point = 6.5

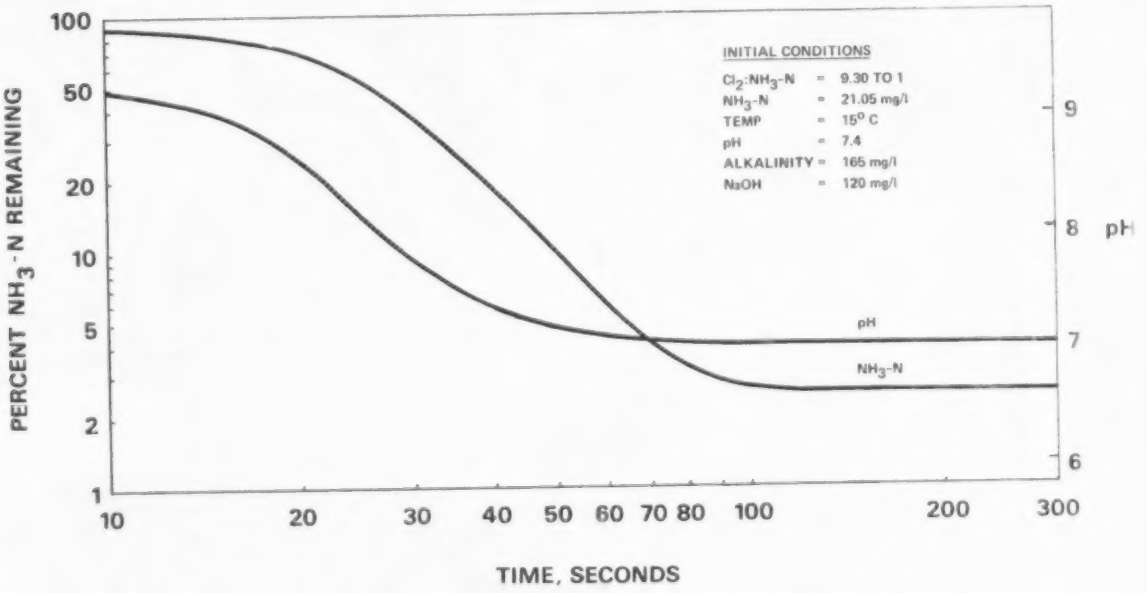

Figure B-2. Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor-Model Prediction-pH Set Point = 7.0

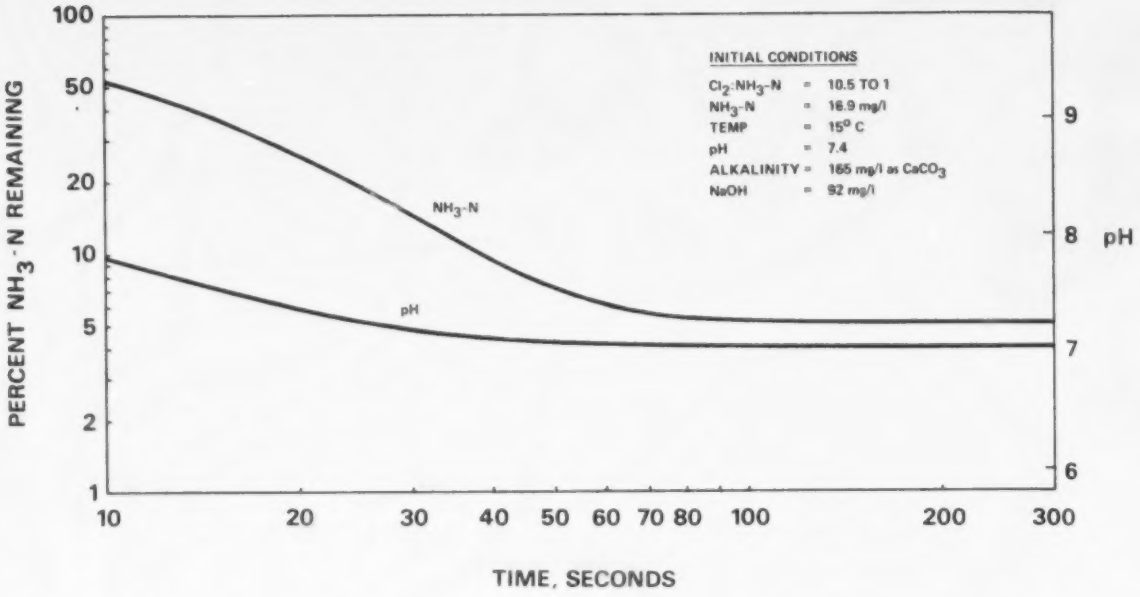

Figure B-3. Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor-Model Prediction-pH Set Point = 7.0

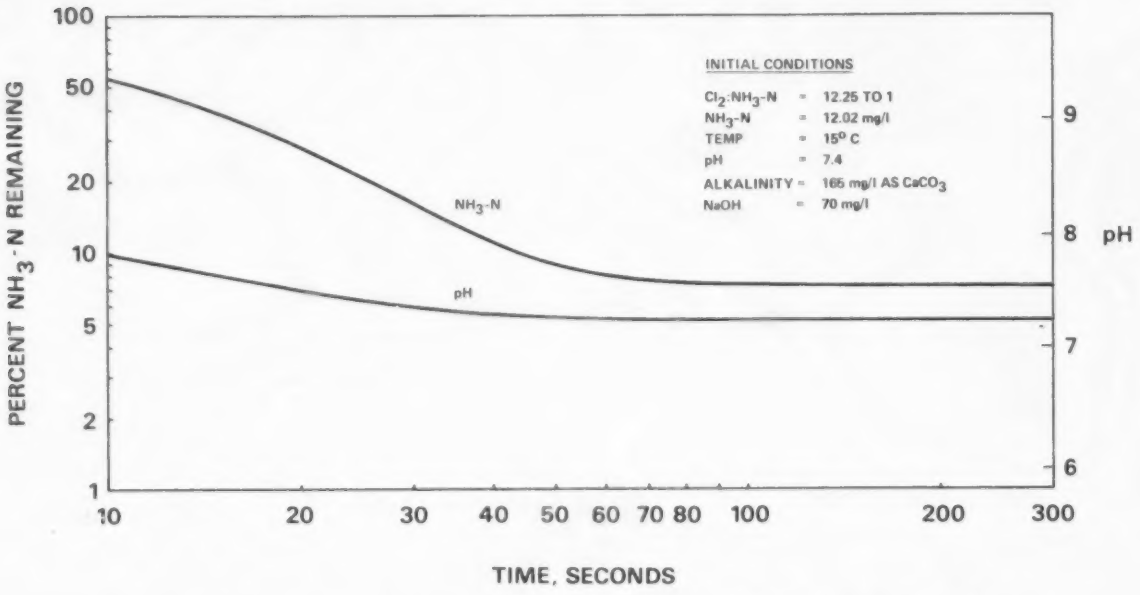

Figure B-4. Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor-Model Prediction-pH Set Point = 7.3

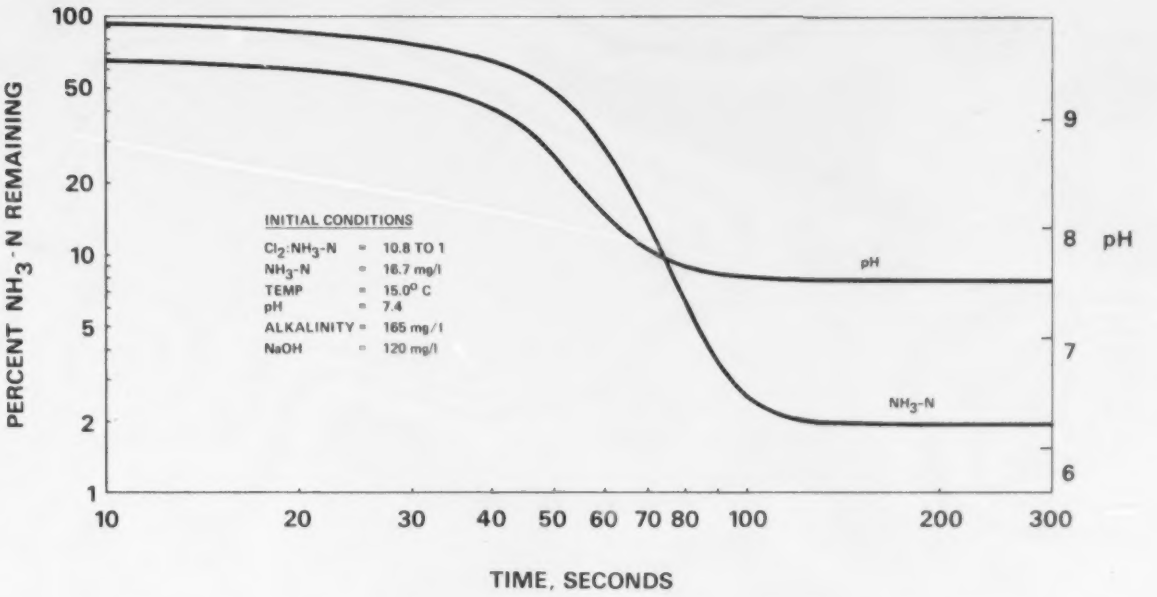

Figure B-5. Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor-Model Prediction-pH Set Point - 7.5

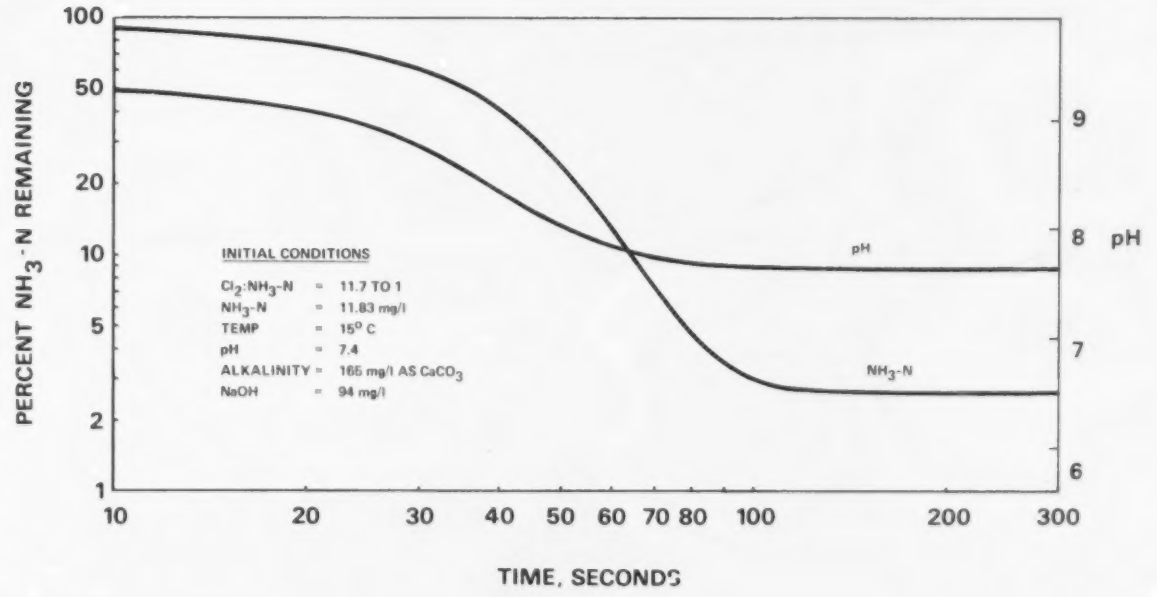

Figure B-6. Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor-Model Prediction-pH Set Point = 7.7

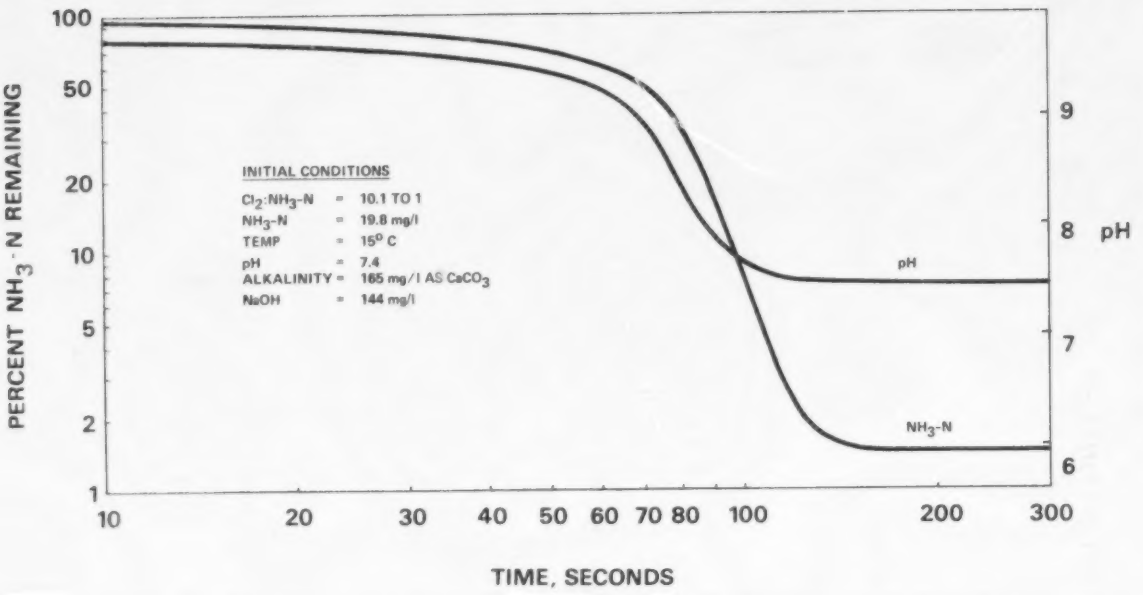

Figure B-7. Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor-Model Prediction-pH Set Point = 8.0

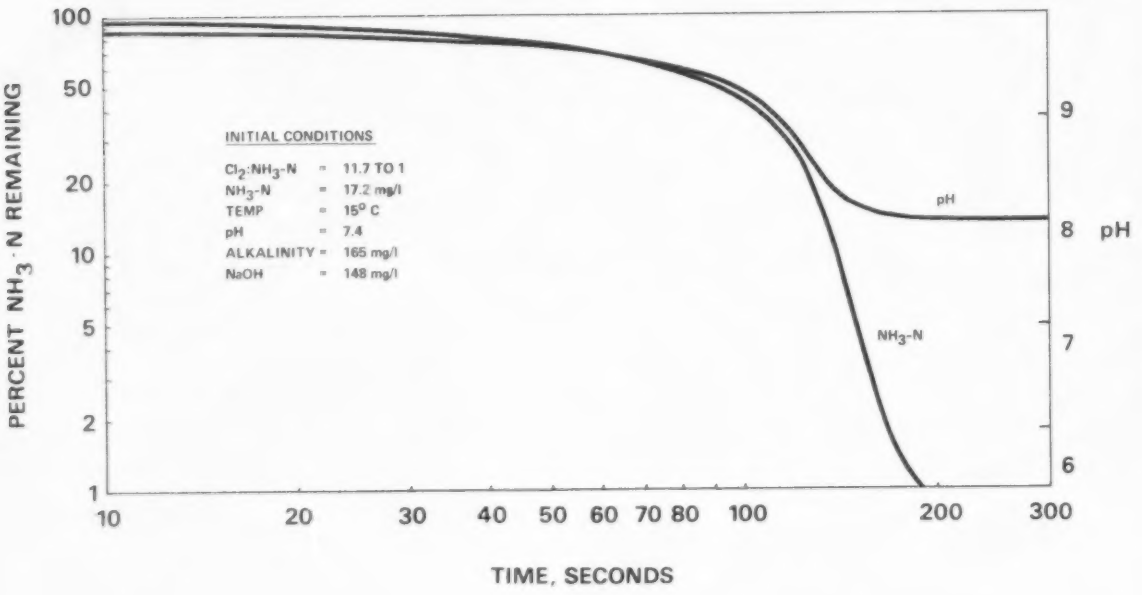

Figure B-8. Ammonia Removal with Breakpoint Chlorination in a Pipe Reactor-Model Prediction-pH Set Point = 8.5

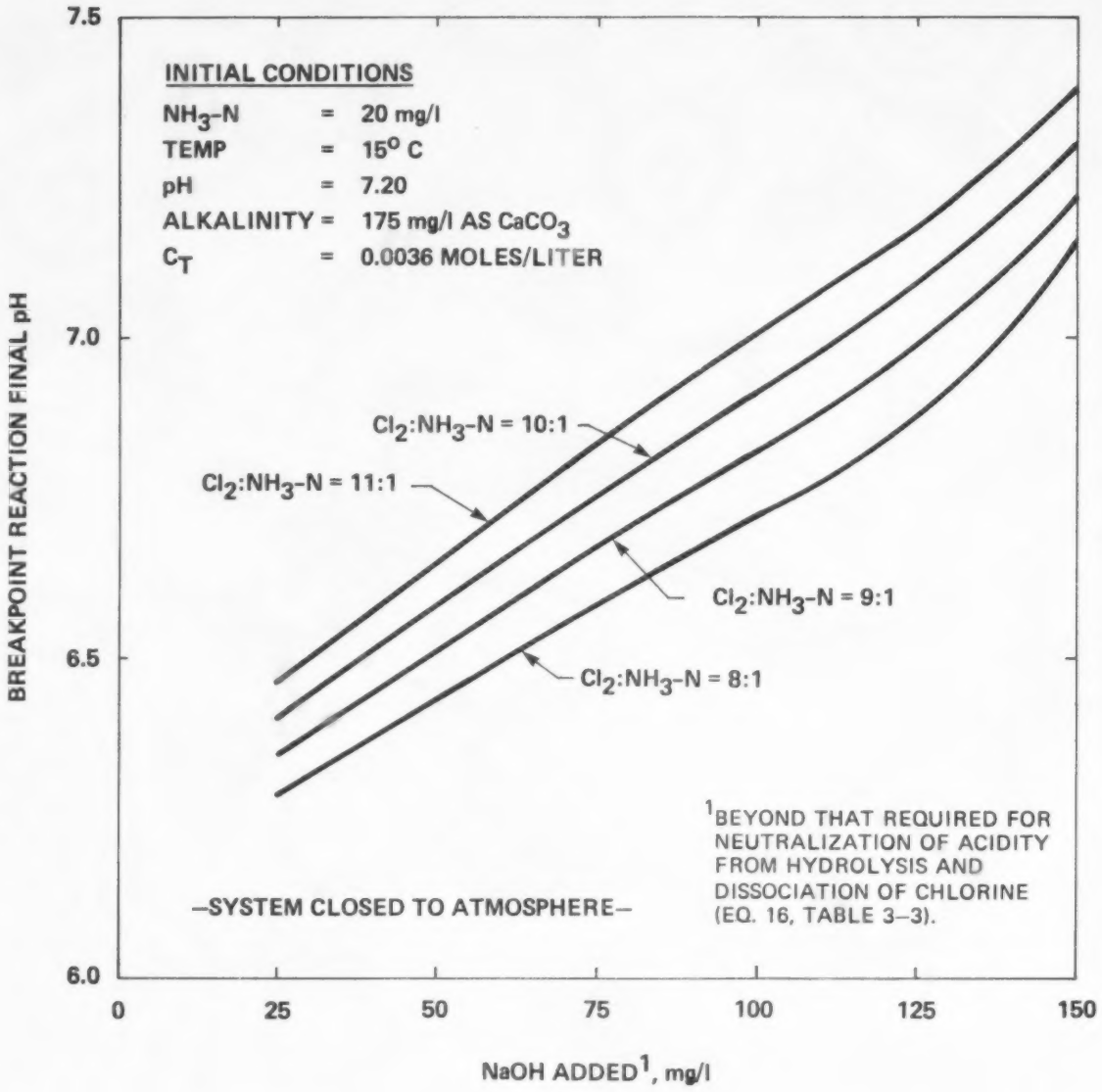

Figure B-9. Breakpoint Reaction Final pH vs NaOH Added, Cl_2:NH_3-N Variable

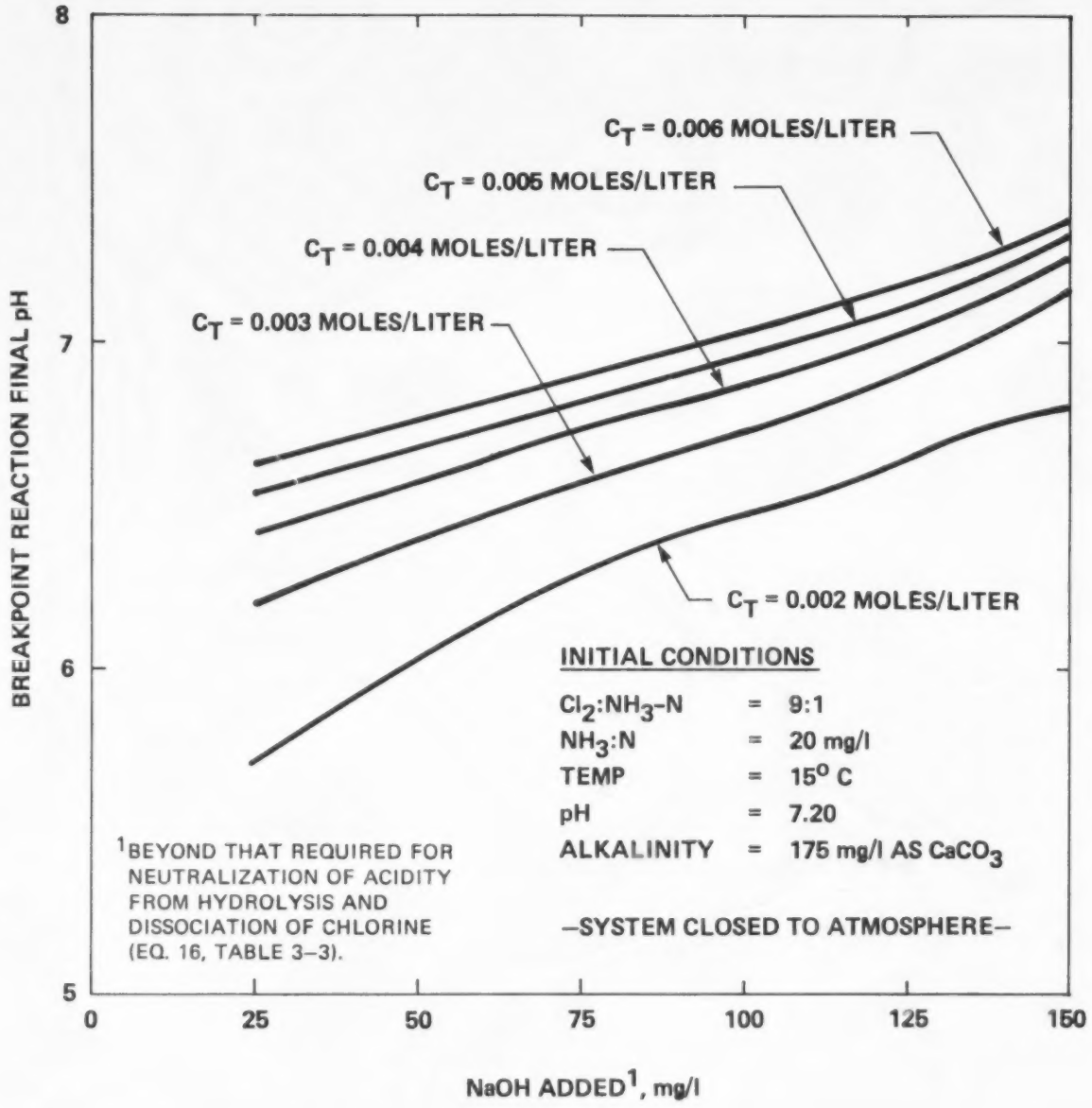

Figure B-10. Breakpoint Reaction Final pH vs NaOH Added, C_T Variable

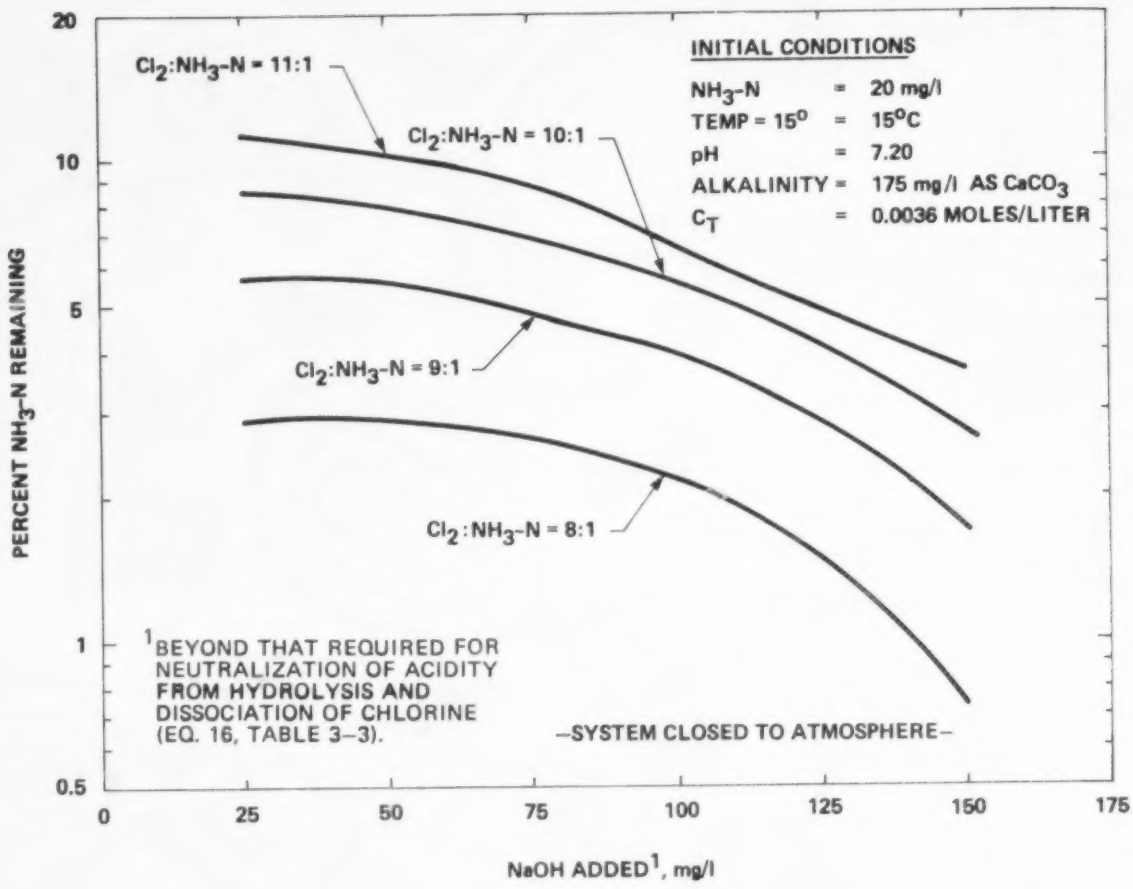

Figure B-11 Ammonia Remaining ($NC1_3$ Formed) vs NaOH Added, $C1_2$: NH_3-N Variable

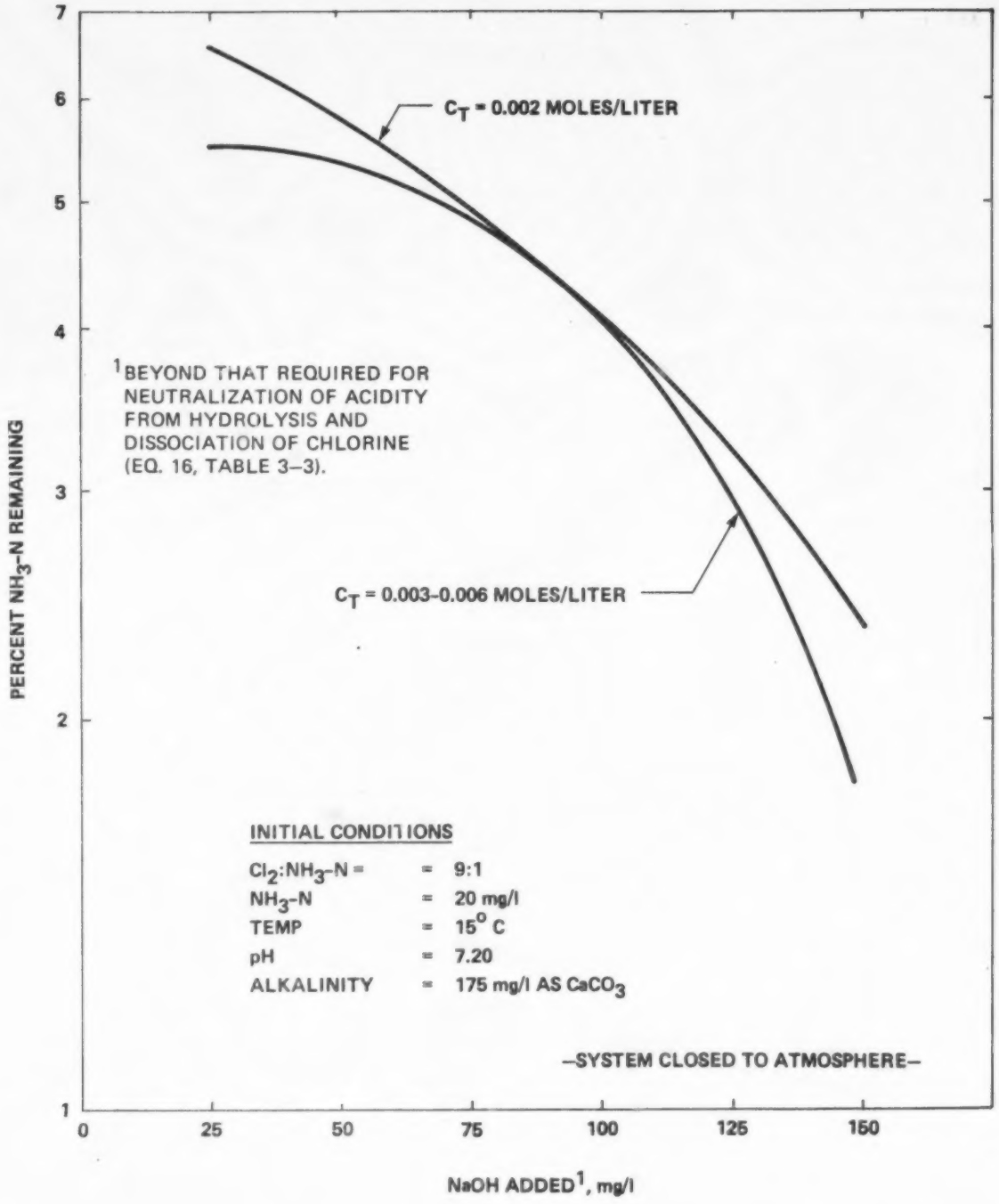

Figure B-12. Ammonia Remaining (NCl_3 Formed) vs NaOH Added, C_T Variable

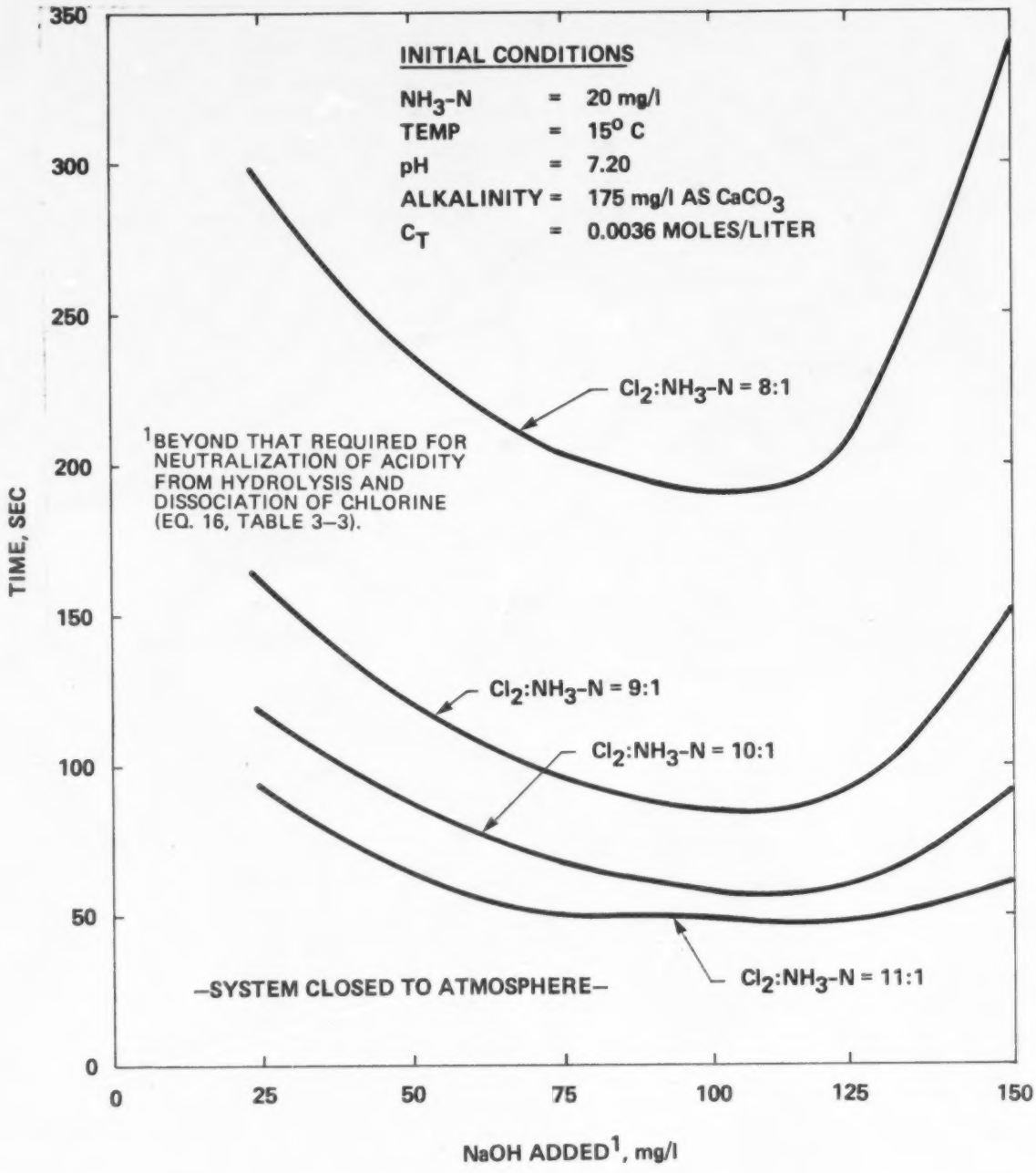

Figure B-13. Time to Reach Minimum Ammonia Concentration vs NaOH Added, Cl_2:NH_3-N Variable

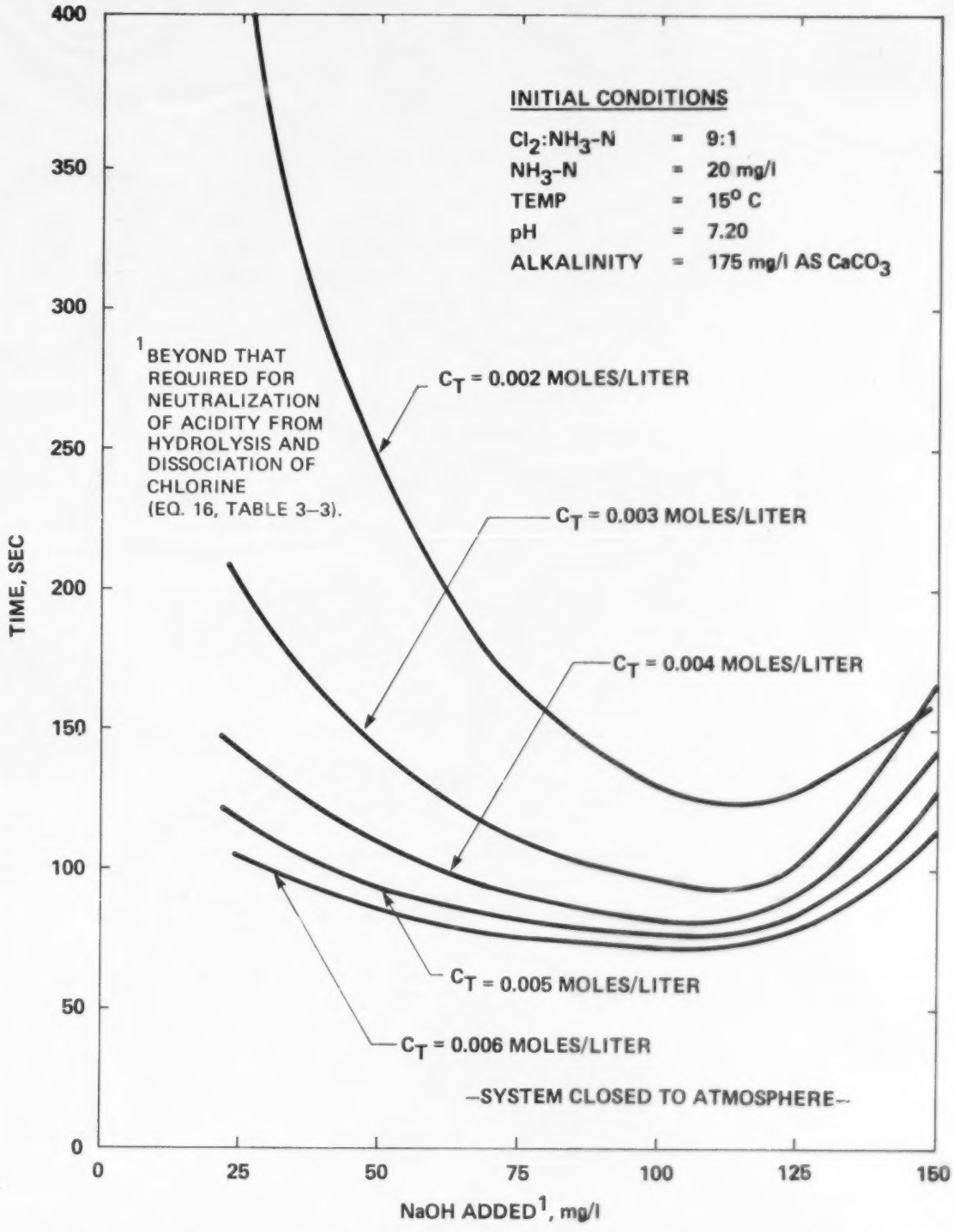

Figure B-14. Time to Reach Minimum Ammonia Concentration vs NaOH Added, C_T Variable

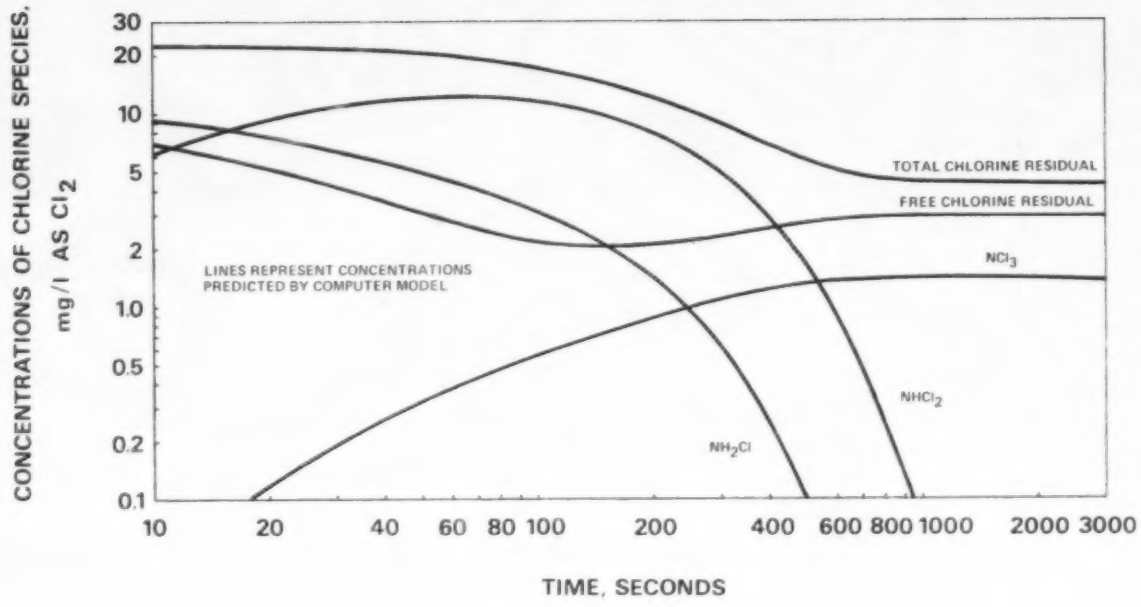

Figure B-15 Predicted Breakpoint Chlorination Kinetics in a Plug Flow Reactor, pH = 6.80, NH_3-N = 2.5 mg/l, Temp = 15 C, Cl_2/N = 9.0

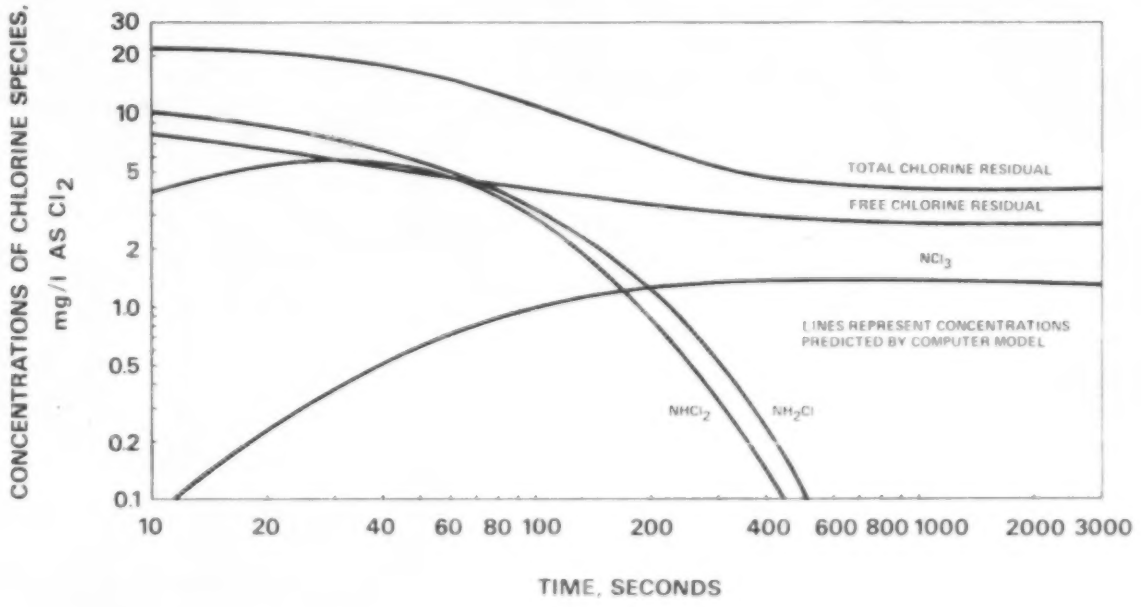

Figure B-16. Predicted Breakpoint Chlorination Kinetics in a Plug Flow Reactor, pH = 7.50, NH_3-N = 2.5 mg/l, Temp = 15 C, Cl_2/N = 9.0